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MATHEMATICS

ON THE ITERATED LOGARITHM LAW FOR HOMOGENEOUS RANDOM PROCESSES WITH INDEPENDENT INCREMENTS

By B. V. GNEDENKO

(Communicated by A. N. Kolmogoroff, Member of the Academy, 26. IV. 1943)

The earlier papers([1]) and ([2]) have been concerned with the determination of the applicability range of the local, as well as of the integral, iterated logarithm law for homogeneous random processes with independent increments. The method used in these papers, however, enabled us to establish only the following:

1) For all homogeneous random processes $\xi(t)$ with independent increments possessing a Gaussian component*, and only for such processes

$$\limsup_{t\to 0} \frac{|\eta(t)|}{\sqrt{2t \lg \lg \frac{1}{t}}} = a, \tag{1}$$

with probability 1, where a is a positive constant $(0 < a < +\infty)$, and $\eta(t) = \xi(t) - \xi(0)$([1]).

2) For all homogeneous random processes $\xi(t)$ of finite dispersion with independent increments, and only for such processes

$$\limsup_{t\to 0} \frac{|\eta(t) - \mathrm{E}\eta(t)|}{\sqrt{2t \lg \lg t}} = a, \tag{2}$$

with probability 1, where a is a positive constant $(0 < a < +\infty)$. In both theorems the meaning of the constant a was not revealed.

The aim of the present publication is to make clear the probability-theoretical meaning of the constant a in formulae (1) (2) and in a general theorem which is a generalization of A. Khintchine's lemma. The latter theorem was the basis of the proofs of the results contained in the above papers.

Theorem 1. *Let $\xi(t)$ be a homogeneous random process of finite dispersion with independent increments, $\eta(t) = \xi(t) - \xi(0)$, $\gamma = \mathrm{E}\eta(1)$. For the given non-decreasing function $u(t)$ and the constant $a\ (0 \leqslant a \leqslant +\infty)$ the equality*

$$\limsup_{t\to 0} \frac{|\eta(t) - \gamma t|}{u(t)} = a$$

* We say that the random variable ξ possesses a Gaussian component, if ξ can be represented as the sum of two independent random variables ξ_1 and ξ_2, one of which follows the Gaussian law with non zero dispersion.

holds with probability 1 if and only if the integral

$$\int_1^\infty P\{|\eta(t)-\gamma t|>cu(t)\}\frac{dt}{t}$$

is convergent or divergent according as $c>a$ *or* $c<a$ (c *is a constant*).

Putting $a=0$, we obtain Khintchine's lemma.

Theorem 2. *If* σ^2 *is the dispersion of* $\eta(1)$, *then in formula* (2) $a=\sigma$.

The proof of this theorem is based upon Theorem 1 and the following lemma that is an analogue to a well-known Kolmogoroff's Lemma ([3]).

Lemma. *If the logarithm of the characteristic function of* $\eta(1)$ *is of the form*

$$\lg f(z,\ 1)=i\gamma z+\int_{-b}^{b}\{e^{izx}-1-izx\}\frac{dG(x)}{x^2},$$

where $G(x)$ *is a non-decreasing function of bounded variation and* $b>0$, *then*

$$P\{|\eta(t)-\gamma t|>x\}<\begin{cases} e^{-\frac{x^2}{2tg}\left(1-\frac{xb}{2t}\right)} & \text{for } 0<x<\frac{4t}{3b}g,\\ e^{-\frac{x}{4b}} & \text{for } x>\frac{t}{b}g,\end{cases}$$

where $g=G(b)-G(-b)=D\eta(1)$.

Theorem 3. *If* σ^2 *is the dispersion of the Gaussian component of* $\eta(t)$, *then in formula* (1) $a=\sigma$.

Proof. Suppose that $\eta(t)=\eta_1(t)+\eta_2(t)$, where the processes $\eta_1(t)$ and $\eta_2(t)$ are independent, $\eta_1(t)$ follows the Gaussian law and $\eta_2(t)$ contains no Gaussian component.

For the sake of brevity denote $u(t)=\sqrt{2t\lg\lg 1/t}$.

It is known [see ([4]) and ([1]) respectively] that

$$\limsup_{t\to 0}\frac{|\eta_1(t)|}{u(t)}=\sigma \tag{3}$$

$$\limsup_{t\to 0}\frac{|\eta_2(t)|}{u(t)}=0 \tag{4}$$

with probability 1. Since with the same probability

$$\limsup_{t\to 0}\frac{|\eta_1(t)|}{u(t)}-\limsup_{t\to 0}\frac{|\eta_2(t)|}{u(t)}\leqslant\limsup_{t\to 0}\frac{|\eta(t)|}{u(t)}\leqslant$$
$$\leqslant\limsup_{t\to 0}\frac{|\eta_1(t)|}{u(t)}+\limsup_{t\to 0}\frac{|\eta_2(t)|}{u(t)},$$

we may conclude from (3) and (4) that in formula (1) $a=\sigma$ with probability 1.

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MATHEMATICS

ON AN ORTHOGONAL SYSTEM

By N. P. ROMANOV

(Communicated by S. L. Soboleff, Member of the Academy, 24. IV. 1943)

The present paper is devoted to the investigation of a special orthogonal system obtained by orthonormalization of the system of functions

$$\Theta_n(x) = nx - [nx]$$

on the interval (0, 1). The functions $\psi_n(x)$ of this system are connected with the functions $\Theta_n(x)$ of the initial system by a remarkably simple relation, viz.

$$\psi_n(x) = \frac{\sqrt{12}}{\sqrt{\varphi_2(n)}} \sum_{d/} \mu\left(\frac{n}{d}\right) \Theta_d(x)\, d,$$

where the summation is extended over all divisors d of the number n and

$$\varphi_2(n) = \sum_{d/n} \mu\left(\frac{n}{d}\right) d^2$$

is the well-known generalized Euler function satisfying the condition

$$\sum_{d/n} \varphi_2(d) = d^2.$$

The proof of the above relations is based upon the investigation of some determinants of the form $|(i, k)^2|$, where (i, k) is the greatest common measure of i and k, as well as upon the formula

$$\int_0^1 \Theta_a(x)\, \Theta_b(x)\, dx = \frac{(a, b)^2}{12ab},$$

which can be found, for instance, in «Lectures on the Theory of Numbers» by E. Landau (vol. II). The analogous considerations enable us to define an orthogonal system $\psi_n^*(x)$ generated by the functions

$$\Theta_n^* = (nx - [nx])^2 - (nx - [nx]) + \frac{1}{6},$$

or, in general, a system $\psi_{n;k}(x)$ generated by the system

$$\Theta_{n;k}(x) = B_k(nx - [nx]) \quad (k = 1, 2, 3, \ldots),$$

where $B_k(t)$ is the k-th Bernoulli's polynomial. In all these cases it is possible to establish the relations analogous to those mentioned above. Namely, we have

$$\psi_{n;k}(x)=\frac{1}{\sqrt{2\frac{k!^2}{(2k)!}|B_{2k}|}}\cdot\frac{1}{\sqrt{\varphi_{2k}(x)}}\cdot\sum_{d/n}\mu\left(\frac{n}{d}\right)d^k\Theta_{d;k}(x).$$

The author proves further the completeness of the orthonormal system

$$1,\ \psi_1(x),\ \psi_2(x),\ \ldots$$

in the sense of the metric of $L_2(0,\ 1)$.

Using essentially the same argument, we can prove the completeness of the system

$$1,\ \psi_{1;k}(x),\ \psi_{2;k}(x),\ \ldots.\ \psi_{1;k+1}(x),\ \psi_{2;k+1}(x),\ \ldots$$

The well known Parceval's identity

$$\int_0^1 f(x)^2\,dx=\Big(\int_0^1 f(x)\,dx\Big)^2+\sum_{n=1}^{\infty}(f,\ \psi_{n;k})^2+\sum_{n=1}^{\infty}(f,\ \psi_{n;k+1})^2$$

leads to some identities containing the primes, no one of which is trivial. The author did not succeed in obtaining them in another way. Parceval's relation is thus a powerful source for obtaining relations useful for the theory of numbers.

Although the orthonormal systems just obtained seem to be rather special, they probably will lead to sufficiently general methods in the theory of primes. Thus, the questions concerning the ordinary convergence of Fourier series of a given function $f(x)$ with respect to the ψ at a given point x are rather difficult, and are connected with the theory of Diophantine approximations and with the distribution of Farray's fractions on the interval $(0,\ 1)$. The generating Dirichlet series for $\psi_{n;k}(x)$ are representable by the following formulae:

$$\sum_{n=1}^{\infty}\frac{\psi_{n;k}(x)\sqrt{\varphi_{2n}(x)}}{n^s}=\frac{1}{\sqrt{2\frac{k!^2}{(2k)!}|B_{2k}|}}\cdot\frac{1}{\zeta(s)}\cdot\sum_{n=1}^{\infty}\frac{B_k(nx-[nx])}{n^{s-k}}\qquad(k=1,\ 2,\ \ldots)$$

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PHYSICS

DETERMINATION OF POTENTIAL ENERGY CONSTANTS FOR HALOGEN DERIVATIVES OF METHANE

By B. I. STEPANOV

(Communicated by S. I. Wawilow, Member of the Academy, 30. VIII. 1943)

The general method for calculating vibrational frequencies of polyatomic molecules given by M. Eliashevich (1) was applied to fluorine, chlorine and bromine derivatives of methane.

The secular equation for vibrational frequencies is

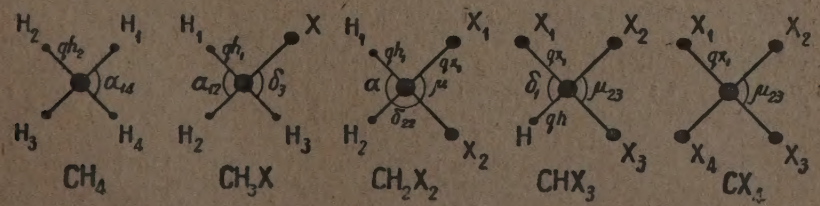
$$\| D_{\alpha} - \omega^2 \delta_{\alpha} \| = 0, \qquad (1)$$

where

$$D_{\alpha\gamma} = \sum_{\beta} A_{\alpha\beta} K_{\beta\gamma},$$

i. e. it is the product of matrices $\| A_{\alpha\beta} \|$ and $\| K_{\beta\gamma} \|$. The first of these matrices, the set of kinematic coefficients, may be easily found for any complicated molecule with the aid of Table 1 in Eliashevich's paper (1), if the numerical values of atomic masses, bond lengths and bond angles are substituted.

The matrix $\| K_{\beta\gamma} \|$, i. e. the set of dynamical constants, should be determined from the vibrational frequencies of the given molecule or of some similar molecules. The calculations provided such type for the cases of methane and ethane(2) with a set of constants which enabled to perform a quite satisfactory evaluation of vibrational frequencies of methane; ethane; propane, buthane and some other molecules (3). The figures thus obtained for the force constants are valuable mainly because they may be used in calculating the vibrational frequencies of the most diversified types of molecule, such as contain equivalent bonds and angles.



The present work was performed in order to determine the set of potential energy constants for halogen derivatives of methane.

In the following formulae expressing the potential energy of these molecules the independent variables are the natural vibrational coordinates, i. e. the changes of the equilibrium values of bond lengths and bond angles (see figure). Thus, the starting point is the valency forces model.

$$CX_4: U = \frac{1}{2}\sum K_X q_{Xi}^2 + \frac{1}{2}\sum K_\mu \mu_{ij}^2 + \sum h_\mu q_{Xi} q_{Xj} +$$
$$+ \sum A_\mu q_{Xi}\mu_{ik} + \sum B_\mu q_{Xi}\mu_{ik} + \sum l_{\mu\mu}\mu_{ik}\mu_{il} + \sum o_{\mu\mu}\mu_{ik}\mu_{jl};$$

$$CHX_3: U = \frac{1}{2}\sum K_X q_{Xi}^2 + \frac{1}{2} K_h q_h^2 + \frac{1}{2}\sum K_\mu \mu_{ik}^2 + \frac{1}{2}\sum K_\delta \delta_i^2 +$$
$$+ \sum h_\mu q_{Xi} q_{Xj} + \sum h_\delta q_{Xi} q_h + \sum A_\mu q_{Xi}\mu_{ik} + \sum B_\mu q_{Xi}\mu_{ik} + \sum A_\delta q_{Xi}\delta_i +$$
$$+ \sum B_\delta q_{Xi}\delta_j + \sum b_\delta q_h \mu_{ik} + \sum l_{\delta\delta}^h \delta_i\delta_j + \sum l_{\delta\mu}\delta_i\mu_{jk} + \sum o_{\delta\mu}\delta_i\mu_{jk} + \sum l_{\mu\mu}\mu_{ik}\mu_{jl};$$

$$CH_2X_2: U = \frac{1}{2}\sum K_X q_{Xi}^2 + \frac{1}{2}\sum K_h q_{hi}^2 + \frac{1}{2}\sum K_\delta \delta_{jk}^2 + \frac{1}{2} K_\alpha \alpha^2 + \frac{1}{2} K_\mu \mu^2 +$$
$$+ h_\mu q_{X_1} q_{X_2} + \sum h_\delta q_{Xi} q_{hl} + h_\alpha q_{h_1} q_{h_2} + \sum A_\delta q_{Xi}\delta_{ik} + \sum B_\delta q_{Xi}\delta_{ik} +$$
$$+ \sum A_\mu q_{Xi}\mu + \sum B_\alpha q_{Xl}\alpha + \sum \alpha_\delta q_{hi}\delta_{ik} + \sum b_\delta q_{hi}\delta_{jk} + \sum \alpha_\mu q_{hi}\mu +$$
$$+ \sum a_\alpha q_{hi}\alpha + \sum l_{\delta\delta}^h \delta_{hiX_1}\delta_{hiX_2} + \sum l_{\delta\delta}^{l} \delta_{h_1 Xi}\delta_{h_2 Xl} +$$
$$+ \sum o_\delta \delta_{hiXj}\delta_{hjXi} + \sum l_{\delta\mu}\delta_{ik}\mu + \sum l_{\alpha\delta}\delta_{ik}\alpha + \sum o_{\alpha\mu}\alpha\mu;$$

$$CH_3X: U = \frac{1}{2}\sum K_h q_{hi}^2 + \frac{1}{2} K_X q_X^2 + \frac{1}{2}\sum K_\alpha \alpha_{jk}^2 + \frac{1}{2}\sum K_\delta \delta_i^2 +$$
$$+ \sum h_\alpha q_{hi} q_{hj} + \sum h_\delta q_{hi} q_X + \sum a_\alpha q_{hi}\gamma_{ik} + \sum b_\alpha q_{hi}\alpha_{jk} +$$
$$+ \sum a_\delta q_{hi}\delta_i + \sum b_\delta q_{hi}\delta_j + \sum A_\delta q_X \delta_i + \sum B_\delta q_X \alpha_{ik} +$$
$$+ \sum l_{\delta\delta}^{l} \delta_i\delta_j + \sum l_{\alpha\delta}\delta_i\alpha_{ik} + \sum o_{\alpha\delta}\delta_i\alpha_{jk} + \sum l_{\alpha}\alpha_{ik}\alpha_{il}.$$

It should be borne in mind that owing to the existence of some relationships between the angles α, δ and μ not all the constants are independent. Nevertheless, even taking these relationships into account, we can hardly succeed in calculating so many constants. Therefore the constants B, b and o, describing the interaction of most distant bonds and angles, were assumed to equal zero, this assumption being in full accordance with the results of calculation of spectra of methane, ethane, propane and buthane.

Using the set of all the remaining unknown constants, secular equations of the type of equation (1) were formed for all the molecules under investigation. These equations will be given in full elsewhere. Moreover, it was supposed that in these molecules all the valency angles are purely tetrahedral. On the basis of such equations with the inserted experimentally known solutions (i. e. Raman and infra-red frequencies) the constants were calculated by the method of successive approximations. Accordingly, the approximate values of constants found for one molecule were introduced into the secular equations of another molecule, and the problem then was to find out how to modify these constants in order to attain a good coincidence between computed and experimentally found frequencies without spoiling thereby the results obtained for the previous molecule. This operation of successive approximations has been applied many times until any further correction of the constants only went to deteriorate the results.

In Table 1 the final values of constants are given. Moreover, the methane constants found previously are given there also. If these constants are made use of in calculating the squares of all the 79 frequencies of these molecules, a very good coincidence with the experimental data is obtained. At the same time I was able to make some corrections in the interpretation of spectra by Ta-You-Wu [4].

As may be seen from Table 1, the force constants vary from bromine to fluorine, and from CH_4 to CX_4 in a regular way. In fluoride derivatives all the con-

Table 1

Potential Energy Constants for the Halogen Derivatives of Methane (in 10^5 cm^{-2})

$X=$	K_X			K_h			K_μ			K_δ			K_α			$-h_\mu$		
	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F
CH_4	—	—	—	—	8.34	—	—	—	—	—	—	—	—	0.71	—	—	—	—
CH_3X	4.7	5.8	9.8	8.53	8.53	8.53	—	—	—	0.95	1.10	1.56	0.73	0.75	0.76	—	—	—
CH_2X_2	4.8	5.9	10.7	8.53	8.53	8.53	1.32	1.61	1.90	0.96	1.11	1.75	0.73	0.76	0.77	0.25	0.45	0.60
CHX_3	4.9	6.1	10.9	8.53	8.53	8.53	1.34	1.62	2.28	0.975	1.12	1.76	—	—	—	0.25	0.45	0.60
CX_4	5.0	6.2	12.3	—	—	—	1.36	1.63	2.47	—	—	—	—	—	—	0.25	0.45	0.65

$X=$	$-h_\delta$			h_α			A_μ			A_δ			a_δ			a_α		
	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F
CH_4	—	—	—	—	0.05	—	—	—	—	—	—	—	—	—	—	—	0.35	—
CH_3X	0.10	0.15	0.30	0.05	0.05	0.05	—	—	—	0.65	0.80	1.25	0.45	0.50	0.90	0.35	0.35	0.35
CH_2X_2	0.10	0.15	0.30	0.05	0.05	0.05	0.80	0.95	1.30	0.80	0.95	1.30	0.50	0.60	1.10	0.35	0.35	0.35
CHX_3	0.10	0.15	0.40	—	—	—	0.85	1.00	1.70	0.85	1.00	1.50	0.50	0.60	1.40	—	—	—
CX_4	—	—	—	—	—	—	1.00	1.15	1.80	—	—	—	—	—	—	—	—	—

$X=$	l_μ			$l_{\mu\delta}$			$l^x_{\delta\delta}$			$l^h_{\delta\delta}$			$l_{\alpha\delta}$			l_α		
	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F	Br	Cl	F
CH_4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.035	—
CH_3X	—	—	—	—	—	—	0.06	0.08	0.13	—	—	—	0.05	0.06	0.12	0.035	0.035	0.035
CH_2X_2	—	—	—	0.07	0.08	0.25	0.06	0.08	0.15	0.11	0.16	0.50	0.07	0.07	0.13	—	—	—
CHX_3	0.10	0.14	0.23	0.09	0.10	0.35	—	—	—	0.13	0.17	0.65	—	—	—	—	—	—
CX_4	0.10	0.14	0.29	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Transition factor to dyne/cm 6.37×10^4 was calculated with the value of effective mass m_h=1.088, according to Hemptinne and Mannebak([5]).

stants have very large values. In particular, the constant of elastic bond C — F even exceeds the constant of elastic bond C — H. From the tabulated data an estimation of the fitness of the valency forces' model may be made.

In the literature we find repeated attempts to confine the calculations to the diagonal elements of potential energy, or at least to a very small number of non-diagonal elements. The total inadequacy of this approximation has already been proved even in the case of methane and ethane. A striking case in point is that of halogen derivatives of methane. The interaction constants of bonds and angles are very large and sometimes very close to the elastic constants of angular vibrations.

In order to check the central forces' model all the coefficients were recalculated. It turned out that this model gave a still less satisfactory correspondence with reality.

Table 2

Comparison of the Observed and Calculated Frequencies for Halogen Derivatives of Methane (ω in cm^{-1}, ω^2 in 10^6 cm^{-2})

	Type of vibration	Br			Cl			F		
		$\omega_{obs.}$	$\omega^2_{obs.}$	$\omega^2_{calc.}$	$\omega_{obs.}$	$\omega^2_{obs.}$	$\omega^2_{calc.}$	$\omega_{obs.}$	$\omega^2_{obs.}$	$\omega^2_{calc.}$
CX_4	E μ	125	0.016	0.015	217	0.047	0.047	437	0.19	0.192
	F μ	183	0.033	0.033	313	0.098	0.098	630	0.40	0.393
	A q_X	265	0.070	0.078	459	0.21	0.232	904	0.82	0.817
	F q_X	667	0.45	0.449	790	0.62	0.625	1265	1.60	1.608
CHX_3	E μ	154	0.024	0.021	262	0.069	0.066	508	0.26	0.256
	A μ, δ, q_X, q_h	222	0.049	0.067	366	0.13	0.133	697	0.49	0.505
	A q_X, μ, δ	539	0.29	0.261	668	0.45	0.453	937	0.88	0.902
	E q_X	655	0.43	0.449	761	0.58	0.616	1116	1.25	1.234
	E δ	1144	1.31	1.297	1215	1.48	1.480	1376	1.89	1.931
	A q_h	3021	9.13	9.167	3019	9.11	9.126	3062	9.38	8.751
CH_2X_2	A_1 μ, δ	173	0.030	0.048	284	0.081	0.104	532	0.28	0.285
	A_1 q_X	276	0.33	0.308	700	0.49	0.470	1078	1.16	1.140
	B_2 q_X	638	0.41	0.414	736	0.54	0.558	—	—	1.368
	B_1 δ	806	0.65	0.680	896	0.80	0.832	1261	1.59	1.594
	A_2 δ	1090	1.19	1.190	1149	1.32	1.320	1294	1.68	1.706
	B_2 δ	1183	1.40	1.432	1266	1.60	1.638	1508	2.27	2.317
	A_1 α, δ	1390	1.93	1.940	1425	2.03	2.010	1508	2.27	2.290
	A_1 q_h	2988	8.93	8.979	2985	8.91	8.971	2964	8.78	8.924
	B_1 q_h	3054	9.33	9.325	3046	9.28	9.287	3029	9.17	9.138
CH_3X	A q_X	610	0.37	0.354	732	0.54	0.535	1049	1.10	1.123
	E δ	957	0.92	0.910	1020	1.04	1.052	1200	1.44	1.461
	A α, δ	1306	1.71	1.694	1355	1.84	1.849	1476	2.18	2.169
	E α	1450	2.10	2.097	1460	2.13	2.154	1476	2.18	2.174
	A q_h	2973	8.84	8.850	2967	8.80	8.847	2965	8.79	8.908
	E q_h	3061	9.37	9.343	3047	9.28	9.331	2987	8.92	9.267

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TECHNICAL PHYSICS

TEMPERATURE AND DEGREE OF IONIZATION OF THE GAS IN IMPULSE DISCHARGE

By S. J. BOGDANOV and K. S. WULFSON

(Communicated by S. I. Wawilow, Member of the Academy, 25. VI. 1943)

The subsequent experiments have shown that the peculiar modifications of the general character of spectra, observed by us when studying the spectrum recording motion films in krypton filled lamps (1); take place in argon lamps as well.

This enables to believe that the essential increase of spark line intensities with the increase of power of disharge, as well as the fact that the luminescence of spark lines comes to an end earlier than that of arc lines, are due to some definite mechanism.

It may be supposed that the difference in behaviour of spark and arc lines is caused by the difference in excitation functions of both kinds of lines. However, the calculations by S. J. Bogdanov have shown that the difference of shapes of excitation functions does not permit to interprete correctly the experimental facts; and; in particular, those modifications which had been observed in spectrum recording motion film when the capacity feeding the impulse lamp is increased or decreased (v_e =const).

When the capacity is decreased, the duration of flowing of the current across the lamp is decreased as well, and therefore, if the relation between the intensities were determined by excitation functions, the time interval between the maximum values of intensity of spark and arc lines would diminish also. As a matter of fact, it does not. Experiment shows that the time interval between the maximum values of spark and arc line intensities, far from decreasing, even grows larger.

Our point of view as expressed below on the mechanism of impulse discharge depends essentially upon the fact that the current intensities at which the prevalence of spark lines over arc lines is observed decrease with the pressure of gas in the lamp*.

The huge power released within the lamp when the swift ($5—10\times10^{-6}$ sec.) impulse currents flow across it, leads naturally to the supposition that very high temperatures and degrees of polarization are established within the lamp. It seems therefore to be of some interest to estimate; even very approximately, the possible energy balance within the lamp, and to compare it with other data secured by the investigation of electrical parameters of impulse lamps.

The quantity of energy released within the lamp may be determined either by measuring the electrical parameters (voltage, current, resistance, etc.), or calorimetrically (2).

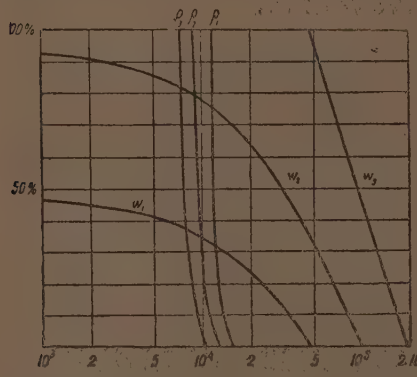
* Basing on this fact one might determine the gas pressure in a preliminarily calibrated sealed vessel.

Owing to the short duration of the discharge, no energy is lost by it, except on radiation. Special measurements have shown that this loss does not exceed 10—20% of the supplied energy. Therefore, the main part of the energy must be spent on heating and ionization of the gas. On these assumptions we may write down the energy balance equation *:

$$W = W_{\text{appl.}} - W_{\text{rad.}} = n\left(\frac{3}{2}kT_{\text{at.}} + \frac{3}{2}kxT_{\text{el.}} + Ax\right), \qquad (1)$$

where W is the energy released per 1 cm³ per whole impulse; n is the number of atoms per 1 cm³ under given conditions; x is the degree of ionization; A, the work of ionization per one atom in eal.

The precise relation between the electron temperature T_{el} and the gas temperature T_{at} is unknown. Two suppositions are possible: 1) the temperature of atoms and ions is much lower than that of electrons; 2) the temperature of atoms and ions is equal to electronic temperature. Strictly speaking, atoms and ions may also differ in temperature to some extent. But not to such an extent as to essentially affect our calculation which is intended to give an approximate estimate only.



W_1=0.2 joule per cm³; W_2=0.4 joule per cm³; W_3=0.8 joule per cm³; $\rho_1=3\times10^{-2}$ Ω cm; $\rho_2=4\times10^{-2}$ Ω cm; $\rho_3=5\times10^{-2}$ Ω cm

We are interested in the determination of the possible lower limits of $t°$ and degree of ionization. Therefore we choose the second supposition. Moreover, the supposition of a high gas temperature is supported by the considerable widening of arc lines observed when the power is increased **.

On the figure the curves W_1, W_2 and W_3 are plotted according to equation (1) for a lamp (d=1 cm³, l=50 cm), filled with krypton, pressure 5 mm Hg. As may be seen from the curves, at $W=0.8$ joule per cm³ the quantity of energy is sufficient not only to give 100 per cent ionization, but to heat the gas up to the temperature of ca. 47 000°.

In order to determine the partition of energy between the ionization and heating we must have another relation involving both these quantities. As one of such relations we may use the equation deduced by Moller(4) on the basis of the formula obtained by Gvosdover (5) for cross-section of a singly charged ion:

$$\rho = \frac{1.48\times10^4}{T_{\text{el.}}^{3/2}} \lg \frac{0.72\times10^6 T_{\text{el.}}^2}{N^{3/2}}, \qquad (2)$$

Equation (2) enables to express the specific resistance of the discharge by means of electronic temperature and concentration of electrons within the gas (for the case when ionization exceeds 10—20 per cent). Measurements of specific ionization of the gas in high power impulse discharge performed by several methods (6) *** have shown that it is very small and depends both on conditions

* Equation (1) pertains to the moment when the releasing of energy W is finished and no noticeable dissipation in surrounding medium has yet taken place. Equation (1) does not take into account the possibility of multiple ionization, since for the powers used in our experiments the number and intensities of Kr III and Kr IV lines were small.

** In a recently published work by E. Frish(3) an opposite situation was observed. As the current densities of stationary discharge increased, the spark lines suffered stronger widening than the arc ones, and moreover Doppler effect took place. It seems to be of most interest to clear up the cause of such a contradicting behaviour of spark and arc lines in stationary and impulse discharges.

*** A more detailed communication will be published elsewhere.

of the discharge and the nature of the gas, and within some limits on its pressure.

This fact which seems at first surprising may also be explained satisfactorily by the high degree of ionization. Putting the specific resistance at 2—4 ohms per cm (this value has been found by experiment), we may, using equation (2), plot the curves ρ_1; ρ_2, ρ_3. Their intersection with the energy curves W_1; W_2, W_3 gives the required solution of the problem; although, of course, very approximately.

The graphical solution of equations (1) and (2) thus found, supports our original suppositions, viz. that the temperature and degree of ionization of the gas are both very high under powerful impulse discharge.

Using the curves of the figure, we may try and trace the development of the process in time. Direct oscillographical measurements have shown that the resistance is almost constant throughout the major part of the duration of the impulse*.

The energy released in the discharge increases with time until all of the energy stored in the condenser goes over into the gas. Therefore the point representing on the figure the state of the gas will move upwards along the resistance curve ($\rho = \text{const}$), passing from one energy curve to another corresponding to a higher energy.

The steepness of the curves ρ indicates that a high electronic temperature is established even in the early stages of the discharge. This seems natural, since the electrons are accelerated in the external field earlier than the ions. In the further stages of the discharge only the temperature of ions and atoms and the degree of ionization are growing**. These quantities attain their maxima when all the energy stored in the condenser goes over into the gas.

The experiment supports this conclusion. The current and luminosity curves as functions of time, obtained by means of a cathode oscillograph, show that the maximum of luminosity of spark lines does not coincide with that of the current, occurring somewhat later, when nearly all the energy has been absorbed by the gas.

The higher the power of the discharge, the earlier the luminosity maximum of spark lines is obtained. Such point of view on the course of the process is confirmed by the similarity of the time variation of luminosity in all the spark lines.

If the electronic temperature changed considerably in course of the discharge, we might expect the maximum of intensity to occur later in spark lines starting from higher levels. However, no such effect is observed on the spectrum recording motion films (1).

All the experimental evidences given above; as well as the quantitative estimation of the part of different processes in impulse discharge enable us to represent the mechanism of such discharge as follows. In the first moments after the breakdown the electrons move with velocities due to action of electric field, and their temperature attains very high values. During the subsequent time interval the degree of ionization and the temperature of the gas begin to increase, because of the collisions of electrons with atoms and ions. As the degree of ionization grows, so does also the intensity of spark lines, for the number of ions becomes larger than that of neutral atoms; moreover, owing to the very high energy of electrons, the process of ionization becomes moreprobable than those of excitation.

When the discharge vanishes, a gradual recombination of ions and electrons sets in, this being accompanied by the radiatioh of a continuous background and of arc lines.

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* When the present work had already been prepared for print, a paper by Murphey and Edgerton (7) appeared, also describing measurements of the volt-ampere characteristics of impulse lamps, these characteristics showing very little deviation of resistance from the constant value, as well.

** On this consideration we must, of course, reject the above assumption that $T_{el} = T_{at}$.

Later on the gas temperature gradually decreases, and that portion of energy which still remains in the gas is through heat conduction and convection given up to the walls of the tube and dissipates in the surrounding space.

In order to get more detailed pictures of the phenomena in the impulse discharge, it is necessary in the further experiments to obtain more rigorous results by means of more precise measurements of the energy and the resistance, and moreover by direct experiments to determine the temperature and the degree of ionization under different conditions of impulse discharge.

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TECHNICAL PHYSICS

RADIOGRAPHY OF EXPLOSION AND DETONATION PROCESSES

By V. A. ZUCKERMAN

(Communicated by E. A. Chudakov, Member of the Academy, 10. VI. 1943)

The experimental study of phenomena that arise on explosion within the explosive and in its immediate neighbourhood presents great difficulties. The shortness of the process and the high temperatures and pressures developed by it preclude the use of ordinary electrical or mechanical indicators. On the other hand, the optical methods of investigation ([1–3]) are confined to observations of the incandescent explosion products (motion pictures, spark photography), or to studying the wave produced by the explosion in the air surrounding the charge (Tepler's method). For analysing the process taking place in the explosive itself or on its boundary a new method has been developed by the author; high speed radiography of explosion and detonation processes.

The possibility of obtaining very intense X-ray «flashes» of as short a duration as one millionth of a second, when the discharge of the condenser is effected through a special mercury poole X-ray tube, was first demonstrated by Kingdom and Tanis ([4]) in 1938. Using similar tubes with mercury vapour for the neutralization of the volume charge Steenbeck ([5]) carried out an X-ray examination of rapidly moving objects. Slack and Ehrke ([6]) have used to advantage the ejection of electrons under the action of a high voltage field and designed discharge X-ray tube with a cold cathode (field emission X-ray tube). Oosterkampf ([7]) has availed himself for the same purpose of a powerful electronic cathode. The author and Avdeenko ([8]) have simplified Oosterkampf's method by using the standard kenotrone as an discharge X-ray tube for microsecond photographs.

All the available methods of spark radiography suffer from a general disadvantage: the quantity of electricity transmitted through the tube by one discharge of the condenser is not above several milliamperseconds. The fusion of the target, the transition of the discharge in the tube into a low voltage arc and the strong drop of voltage due to the self-induction of the lead-in conductors, all these are the principal factors in limiting the energy of a single flash-back. On that account only simple objects, having a low density, could be reproduced on radiographs in as short an interval as the duration of a single flash ([4–6]).

This circumstance greatly restricts the application range of microsecond radiography, but is of no such importance for the X-ray picturing of the explosion process. The secondary explosives, the most widely used in engineering (tetryl, trotyl, melinite and others), are all light atom compounds and lend themselves very well to X-ray examination under a low energy of a single flash. The shell of incandescent gases, which interferes so strongly with optical examinations, has no effect whatever, owing to its small density, on the image fixed by an X-ray film. Not so with primary, or initiating explosives (mercury fulminate, lead acid). Their products of explosion contain heavy elements (mercury, lead), and

the images produced are of high contrast with sharply outlined volumes, the products of the explosive reaction were occupying at different stages of its development.

In order to obtain instantaneous X-ray photographs of an explosion it is necessary to protect the camera from the shock wave and secure an exact coincidence in time between the explosion and the taking of the photograph. The first problem is easily solved by enclosing the disharge X-ray tube and the films in armoured casings provided with windows made from duraluminium sheets to let the X-rays through.

In solving the second problem we availed ourselves of the change in the configuration of the positive electrode of the spark gas under the action of the shock wave. For that purpose the positive electrode was made in the shape of a hollow sphere, in which the investigated charge and the plate-holder with the X-ray film were placed. In front of the charge (on the side of the second electrode of the spark gap) a rectangular window was cut out in the wall of the sphere. Before starting the experiment, this window was closed by gluing to it a thin aluminium foil.

Upon the bursting of the explosive the shock wave tears the light foil away. The positive electrode having now changed its configuration, there is also a change in the voltage of the electric field, and the dielectric strength of the gap undergoes a sharp decrease. A spark jumps over between the electrodes, the voltage of the condenser is applied to the poles of the tube, the generation of the X-ray emission takes place and the explosion is pictured on the film. By varying the distance between the charge and the foil we varied the length of the shock wave path and the time at which the spark-over occurred. As the speed of the shock wave at the boundary of the charge is near to the detonation velocity, this method of regulation proved to be very accurate and allowed to fix the explosion upon the film after a specified interval of time had elapsed since the start of the explosive reaction.

In order to determine the velocity of the explosion products and the flying fragments, one more condenser was added to the scheme. It had a spark gap of its own and the foil was placed at a different distance from the charge. In this way we obtained on the X-ray photograph two superimposed images of different phases of the same process. By varying the distance of the foil we could change the moment when the first photograph was taken, and the interval between it and the time of taking the second. With this time interval and the displacement of the images measured, the velocity of every detail of the photograph can be easily found from such a «double» X-ray record.

By this very method were obtained the radiographs given in Fig. 1. They represent an explosion of a mercury-fulminate-tetryl charged detonator No. 8 with a small piece of the detonation fuse. The general arrangement of details in our X-ray photographs is shown in Fig. 1,*a*. At the end of the detonator there were two steel balls, 4 mm in diameter; one by the side of the detonator, the other in the butt-end depression of the tetryl. To the two sides of the detonation fuse two copper wires were attached.

Fig. 1, *b* presents a radiograph of the detonator and the fuse before the explosion. We may clearly see on it (from left to right) the electric starter, the mercury fulminate [$Hg(ONC)_2$] which is completely opaque to rays, the comparatively transparent tetryl, and the mercury-fulminate-tetryl core of the fuse.

Fig. 1,*c* shows the first stage of the explosion. The products of decomposed mercury fulminate are taking up the volume of the disc flattened out along the axis of the detonator. Their speed in radial directions is much higher than along the axis. The distinct boundary between the explosion products of mercury fulminate and of tetryl* is a smooth curve whose ends are bent in toward the mer-

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* The explosion products as well as tetryl itself are sparingly absorbed by X-rays and are not therefore visible on radiographs. Yet, they may be easily made so in the case of investigations of special tetryl charges, by adding salts of heavy metals to tetryl.

cury fulminate. This is probably because the detonation is more energetic and swift in the case of tetryl (2420 cal/litre; V_d=7000 m/sec.) than in that of mercury fulminate (1050 cal/litre; V_d=4000 m/sec.).

The laterally situated ball has moved a little away from the detonator axis. The front ball is broken and its fragments have travelled through a much longer distance, as compared to the path of the lateral ball. The explosive mass of the fuse had time to decompose only within a half of its length. There is quite distinct

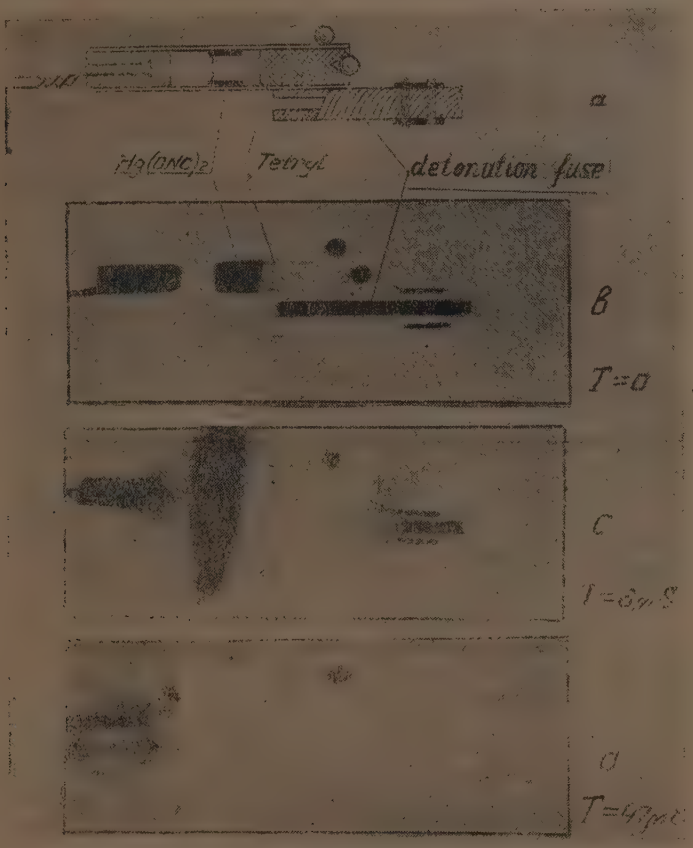

Fig. 1. Radiographs of the detonator explosion with a piece of detonation fuse

boundary between the exploded and the intact portion. It is worthy of note that this phenomenon was observed by me only at the early moments of the explosion of the fuse—1 or 2 cm off the detonator. On those radiograms which have fixed the detonation of the fuse while at a distance of 10—15 cm from the detonator, this boundary is diffused over a length of 20—25 mm. Apparently, when the explosive reaction has only just started, its development along the fuse proceeds at a rate that is many times below that of detonation.

Fig. 1, *d* pictures a later phase of the explosion. The mercury fulminate decomposition products have been pushed well behind and are occupying a small area in the left part of the radiograph. The boundary between them and tetryl is much diffused. Distinctly visible are several fragments of no regular shape from the copper cup, where the mercury fulminate was pressed in. The lateral ball is continuing its movement away from the axis of the detonator. The fragments of the

front ball have travelled far to the right and are taking up a large area. The fuse is decomposed completely.

In order to determine the velocity of every detail on the radiograph of Fig. 1 and the time interval τ elapsed since the start of the explosive reaction, I resorted to the method of double radiographs.

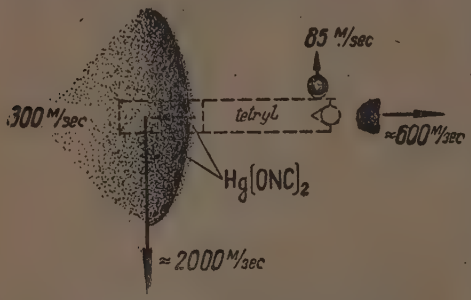

Fig. 2. Velocity diagram of the explosion products of the detonator and the balls. Obtained by method of computing the double radiograph of the details of Fig. 1. By dotted lines is given the position of the detonator and of the balls before the explosion

The results of these measurements are presented diagrammatically in Fig. 2. The fragments of the front ball have been found to move with a speed that is very near to that of a bullet and is 7 or 8 times as high as the speed of the lateral ball. The rate of displacement of the mercury-tetryl boundary along the axis of the detonator is 300 metres per second. This value is many times less than the velocities at which fly the fulminate explosion products in radial directions, which they do at a rate approaching that of detonation for mercury fulminate.

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CHEMISTRY

ON THE SIGNIFICANCE OF THE COEFFICIENTS IN THE FORMULA DETERMINING THE CRYSTALLINE LATTICE CONSTANT OF SOLID SOLUTIONS

By N. V. GRUM-GRZIMAYLO

(Communicated by N. P. Chizhevsky, Member of the Academy, 23. IV. 1943)

In an earlier paper (1) of mine I have given a formula involving the deviation of the constant of a solid solution space lattice from Wegardt's rule. According to this formula, the deviation of the constant from the value prescribed by the rule of Wegardt is proportional to the product of the components' concentration in the solid solution, raised to powers corresponding to atomic indices in the chemical formulae of the crystallochemical compound present in the solid solutions.

The value of the coefficient of proportionality in this formula can be established from statistical laws. In fact, the probability that the atom of the selected component fills up the place assigned to it (whether in the node of the lattice, replacing the atom of the main component, or in the interatomic spaces) is apparently equal to the concentration of the component in the solution, c_{I}; similarly for a second component we have c_{II}; and for an n-th component, c_n.

If the crystallochemical compound of the solid solution contains p atoms of the first component, q atoms of the second and so on, and z atoms of the n-th component, then the probability that all atoms of these components simultaneously fill up their assigned places (thus forming an ordered structure) is:

$$W = c_{\mathrm{I}}^{p} \times c_{\mathrm{II}}^{q} \times \dots \times c_{n}^{z}.$$

In other words, it is equal, just as in the formula for the lattice constant of solid solutions, to the product of the components' concentrations raised to powers corresponding to the indices of the crystallochemical compound.

Making use of Boltzmann's equation, we can write

$$W = e^{\frac{S}{kT}}, \qquad (1)$$

where W is the probability of the state of the crystalline lattice in the above sense; S is entropy; k is Boltzmann's constant referred to the respective number of atoms.

If Q is the thermal energy of the crystallochemical compound in solid solution, T absolute temperature and σ the value of the entropy for $T = 0$, then

$$S = \frac{Q'}{T} + \sigma. \qquad (2)$$

If the heat of chemical interaction between the components is denoted by u and the work expended in the change of the lattice constant by r, we have

$$Q = u + r = u \pm p\Delta V.$$

Here p is the coefficient of elasticity of the crystal in a given direction; ΔV, the change of atomic volume. The atomic volume V is obviously equal to $\frac{\pi^3}{\rho}$, where π is the lattice constant; ρ, the number of atoms in a cell, and

$$\Delta V = \frac{1}{\rho}\left[(\pi + \Delta\pi)^3 - \pi^3\right]. \tag{3}$$

Comparing (1), (2) and (3) we obtain

$$W = e^{\frac{1}{kT}\left[u - \frac{p}{\rho}\left\{(\pi+\Delta\pi)^3 - \pi^3\right\}\right] + \frac{\sigma}{k}} \tag{4}$$

Upon having developed this equation in a MacLaurin series

$$W = e^{\left[\frac{u}{kT} + \frac{\sigma}{k}\right]} \times \left\{1 - \frac{3p\pi^2}{\rho kT}\Delta\pi + \ldots\right\}$$

and taking it up to the first term after unity, let us solve it with respect to $\Delta\pi$:

$$\Delta\pi = -\frac{\rho kT}{3p\pi^2} We^{-\left[\frac{u}{kT} + \frac{\sigma}{k}\right]} + \frac{\rho kT}{3p\pi^2}.$$

Adding to both members of this relation the value of the crystalline lattice constant of the pure main component, we on the left obtain the value of the constant for the given state of the alloy, and on the right, taking into account that the term $\frac{\rho kT}{3p\pi^2}$ may be regarded as a correction for the thermal expansion of the alloy, we obtain

$$\pi = \pi_0 - \left[\frac{\rho kT}{3p\pi^2} e^{-\left[\frac{u}{kT} + \frac{\sigma}{k}\right]}\right] W$$

and the sought for value of the coefficient in the formula for the crystalline lattice constant is

$$A = \frac{\rho kT}{3p\pi^2} e^{-\left[\frac{u}{kT} + \frac{\sigma}{k}\right]}.$$

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3. I. 1943.

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CHEMISTRY

A CHARACTERISTIC OF BAUXITES OF THE VYAZOV DEPOSIT ACCORDING TO HEATING CURVE RECORDS

By J. A. FIALKOV and A. I. TSVETKOFF

(Communicated by V. G. Chlopin, Member of the Academy, 13. V. 1943)

In the north-eastern part of the Bashkirian ASSR, in the Salavat region and the adjoining Satka and Katav regions of the Cheliabinsk district, on the western slope of the South Urals bauxite deposits are located referring to the Palaeozoic (Upper Devonian).

These bauxite deposits were unknown until about 10 years ago. The first information appeared in 1934. At that time Beloussov and some other workers of the Institute of Economic Mineralogy had started a geological investigation of the South-Ural bauxite deposits, which in 1935 resulted in the discovery of the so-called Kuksha deposit now operated on a commercial scale. Near the Kuksha bauxite deposits, along the Yuryuzan and Katava rivers a number of outcrops of bauxites and diaspore-chamosite ores have subsequently been discovered. These bauxite deposits, for the first time investigated (in 1935—1937) by Beloussov(1), Soboleva (2) and Rozhkova (3), have until recently remained insufficiently prospected and little studied.

All the South-Ural bauxite deposits listed above according to their geographical location, as well as to their qualitative characters, may be subdivided into three groups: the Kuksha, Vyazov and Yuryuzan groups. Since 1939 the Vyazov and Yuryuzan deposits were investigated by the Bashkirian Geological Administration (N.D. Sukharev, M. F. Vikulova, M. A. Rebenko, and others), whose work permitted largely to increase the information available.

Chemical investigation and technological sampling of the bauxite rocks of the Vyazov and Yuryuzan deposits made with the purpose of ascertaining the possibilities and ways of their utilization in aluminium industry and some other chemical industries, are being made at the Chemical Intitute of the Academy of Sciences of the Ukrainian SSR (by J. A. Fialkov and his collaborators).

Along with high-alumina bauxites, the Vyazov and especially the Yuryuzan deposits carry also bauxite rocks of an alumina content of the order of 30—40 per cent and of a high content of silica and iron, with a silica modulus less than 2.5 and in some cases even less than 1. This makes us to refer such rocks to allites and siallites.

The first to investigate the mineralogical composition of the bauxite rocks of the South-Ural deposits was Beloussov (1). According to his data, the chief rock-forming minerals of the ores of the deposits named are: diaspore, sedimentary iron silicates (leptochlorites), and hydrous iron oxides, mainly of the hydrohematite type. Accordingly, Beloussov points out the following varieties occurring among the ores of the Yuryuzan and Vyazov deposits: chamosite ores, diaspore-chamosite ores, diaspore-hydrohematite ores, chamosite-hydrohematite ores, and bauxites.

The peculiarities of the mineralogical composition of the ores of the South-Ural bauxite deposits, as pointed out by Beloussov, were deduced by him from a determination of heating curves and from an optical analysis of nine specimens of oolitic ores from the Yuryuzan deposit.

It is noteworthy that Beloussov failed to reveal presence of kaolin in any of the specimens studied; all the heating curves obtained by him are lacking the exothermal effect between 900 and 1000°, characteristic of kaolinite (indistinct traces of the effect have been found in two cases only). Diaspore has been discovered optically nearly in all of the specimens.

The ores of the Vyazov deposit have been very little studied from the mineralogical standpoint. No thermal analysis of these ores has been made. The Vyazov bauxite deposits may, however, be of great commercial importance.

This fact being considered, it was decided to determine the heating curves of ores taken from different areas of the Vyazov deposit. All the samples were sorted out by the geological-prospecting parties of the Bashkirian Geological Administration. Two samples of clays taken from the Ferm and Yuryuzan areas of the Vyazov deposit were also subjected to investigation; at these places bauxite deposits are usually covered by clays.

These investigations were carried out at the Thermal laboratory of the Bashkirian Petroleum Expedition of the Academy of Sciences of the USSR. The thermal analysis—a determination of heating curves—was made with the aid of an apparatus of N. S. Kurnakov's system by the differential method. The thermograms obtained are shown in the figure, Nos. 1—10. The chemical composition, in the table.

The results of the investigation of samples taken at different areas of the Vyazov deposit permit of classing these samples into two groups from the mineralogical standpoint.

To the first group should be referred bauxites with a silica modulus of 5—6. Such are, for instance, samples No. 6/620 from the first Chukur area, No. 7/575 from the Yuryuzan area, No. 52 and No. 53 from the Ferm area.

Thermographs of these samples shown in the figure, Nos. 2, 5, 7 and 8, reveal a predominance or considerable content of diaspore. The kaolinite exothermics is either absent altogether or very slight. According to data of immersion analysis, in the brown earthy mass of rocks an extensive development of diaspore ($N > 1.710$), leptochlorites ($N \sim 1.660$), and occasionally a small admixture of calcite have been noted.

To the second of the above-mentioned groups of bauxite rocks of the Vyazov deposit we assign, from data of thermal and optical analyses, sample No. 4/583 (siallite with a silica modulus of 1.06) and sample No. 8/584 (allite with a silica

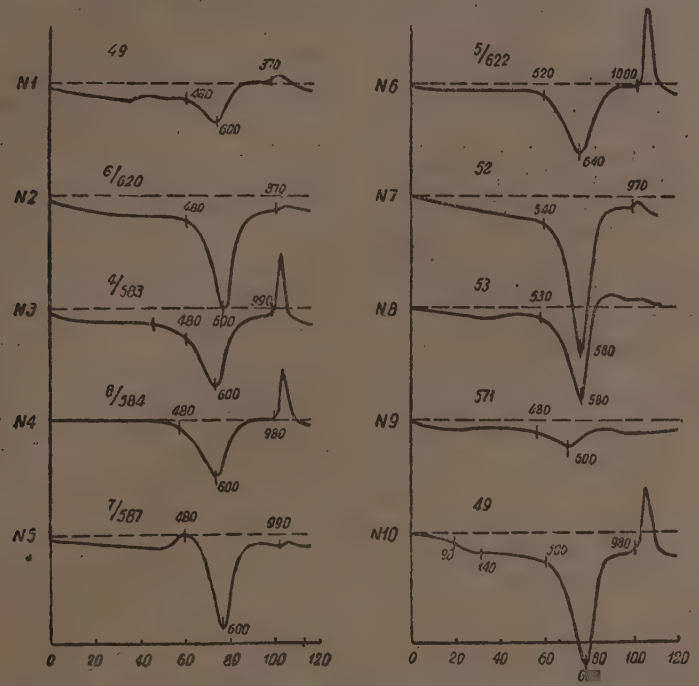
Chemical Composition of the Bauxite and Clay Samples Studied

Nos.	Name of specimen and No. of sample	Area	Chemical composition in per cent							
			Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Loss on ignition	Total	Silica modulus
1	Bauxite 49 (siallite)	Ust-Katav	24.06	30.07	31.52	0.83	0.29	13.60	100.37	0.8
2	Bauxite 6/620	1st Chukur	66.23	11.33	5.80	2.64	0.5	13.60	99.60	5.8
3	Bauxite 4/583 (siallite)	Yuryuzan	36.91	34.50	11.08	2.13	0.5	15.30	99.92	1.06
4	Bauxite 8/584	»	45.52	27.63	10.08	2.13	0.6	14.94	100.30	1.6
5	Bauxite 7/575	»	61.07	10.30	11.84	2.96	0.5	12.98	99.15	5.9
6	Bauxite 5/622 (siallite)	Ferm	33.83	37.90	13.60	1.77	0.5	12.96	100.06	0.9
7	Bauxite 52	»	59.96	12.13	12.05	2.66	0.5	13.18	99.98	4.9
8	Bauxite 53	»	52.43	8.60	25.68	2.42	0.5	10.26	99.39	6.1
9	Clay 571	Yuryuzan	21.69	65.07	5.68	1.16	0.28	5.68	99.56	—
10	Clay 49	Ferm	46.70	23.63	14.15	2.22	0.49	12.74	99.93	—

modulus of 1.6) from the Yuryuzan area, as well as sample No. 5/622 (siallite with a silica modulus of 0.9) from the Ferm area.

The thermographs represented in the figure, Nos. 3, 4 and 6; and the results of optical investigation show that these ores belong to diaspore-kaolinite ores containing a certain amount of leptochlorites.

The results of heating curve determination characterize the bauxite rocks of the Vyazov deposit studied chiefly as diaspore and diaspore-kaolinite rocks,



Differential curves of bauxites and clays of the Vyazov deposit: No. 1, Ust-Katav area; No. 2, sample from the 1st Chukur area; No. 3, sample from the Yuryuzan area; No. 4, sample from the Yuryuzan area; No. 5, sample from the Yuryuzan area; No. 6, sample from the Ferm area; No. 7, sample from the Ferm area; No. 8, sample from the Ferm area; No. 9, clay from the Vyazov deposit; No. 10, clay from the Ferm area

carrying also a certain, generally insignificant, amount of leptochlorites. Thus, by the main mineralogical composition the Vyazov deposit of bauxites differs from the Yuryuzan deposit located in its immediate vicinity.

For the sake of comparison, in the figure, No. 1, a thermograph is given which we have obtained with a sample of green oolite ore (siallite) taken from the Ust-Katav area of the Yuryuzan deposit. The chemical composition, heating curve and optical study show, in agreement with Beloussov's data, that the rock described is composed mainly of sedimentary iron silicates of the leptochlorite type. There is a certain admixture of kaolin, the presence of which is fixed on the thermograph by a exothermal peak at 970°.

The chemical analysis of the clay samples investigated characterizes them as high-silica clays with a SiO_2 content in most cases above 60 per cent. One of the sample was found to contain 73.7 per cent. The optical study of one of such samples (No. 571), the thermograph of which is given in the figure, No. 9, has shown that the essential, if not the principal, component of this particular clay is fragmentary quartz ($N_\omega < 1.547 > N_\varepsilon$).

Among the clay samples investigated, sample No. 49 from the Ferm area is sharply distinguished, containing 46.70 per cent Al_2O_3, 23.63 per cent SiO_2 and 12.7 per cent H_2O.

The heating curve (figure, No. 10) shows three reactions: (1) an endothermal reaction at 90—140,° very slight; (2) an endothermal reaction at 500—600°, very intense, and (3) an exothermal reaction at 980°, also rather intense.

The temperatures of the reaction at 500—600° and 980° correspond to dehydration and conversion of kaolin; the sharp discrepancy of the peak areas, however, points to the presence of diaspore in the rock. Indeed, the recalculation of chemical analysis to minerals gives a kaolin content of about 50 per cent, and that of diaspore 30 per cent, which goes to support the interpretation of the thermograph given above. A slight endothermal effect at 90—100° and hygroscopic humidity.

The results of the investigation permit of assumption of a genetic relation between the clays and the bauxites of the Vyazov deposit.

Such a conclusion may be made, for instance, from a comparison of the results of thermal and immersion analyses of the clay, sample No. 49 (figure, No. 10) and the bauxites, samples Nos. 5/622, 52 and 53 taken from the same Ferm area (figure, Nos. 6—8).

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PHYSICAL CHEMISTRY

STUDY OF THE INTRAMOLECULAR HYDROGEN BOND BY THE METHOD OF COMBINATION SCATTERING OF LIGHT

By M. I. BATUEV

(Communicated by S. I. Wawilow, Member of the Academy, 3. VIII. 1943)

In a previous paper (1) a sharp distinction has been reported between the combination spectra of the hydroxyl group of phenol or *p*-chlorophenol, on the one hand, and *o*-chlorophenol, on the other. The spectrum in the case of the former two substances is a wide band similar to the hydroxyl group band of water or alcohol in the liquid phase; the middle of the band lies about 3410 to 3420 cm^{-1}. In the case of *o*-chlorophenol this spectrum is characterized by a sharply narrowed band; the peaked maximum whereof lies at 3535 cm^{-1}, i. e. it is displaced in the direction of high frequencies with regard to the position occupied by the middle of the respective band of phenol or *p*-chlorophenol by over 100 cm^{-1} (Table 1 and Fig. 1).

The wide OH band of phenol, or *p*-chlorophenol is explained by the oscillations of the hydroxyl group disturbed by the adjacent molecules in the process of formation of associated complexes on the basis of the intermolecular hydrogen bond O—H... O.

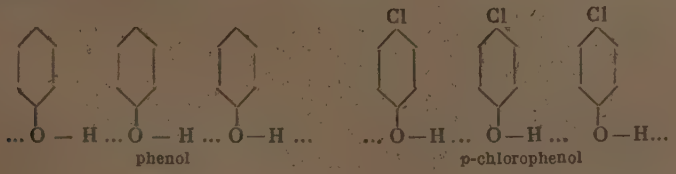


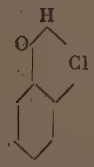
Table 1

Position of the Middle of the Band and the Breadth of the OH Group Band of Phenol, *o*- and *p*-Chlorophenol, in cm^{-1}

Substance	Frequency	Breadth of the band*
Phenol	3410±15	250
p-chlorophenol . .	3420±15	300
o-chlorophenol . .	3535±15	120

*An approximate measurement of the band on the microphotograph obtained by means of the exciting triplet: 27388, 27353, 27293 cm^{-1}.

As the reason for the sharp narrowing of OH band in the case of *o*-chlorophenol we suggested the predominance in this substance of unassociated molecules protected from interaction with the adjacent molecules by intramolecular hydrogen bond O—H... Cl (chelate ring) formed according to the scheme:



In this paper these assumptions have been confirmed and developed further.

To begin with, it should be investigated whether or not the peculiar properties of the spectrum of the hydroxyl group of *o*-chlorophenol may have its cause in the ortho-structure of the molecule. With this object in view we have studied the spectra of *o*-cresol and *p*-cresol, since for these two substances the intramolecular ring-closure is out of the question and, therefore, the effect of ortho- and para-structure should be displayed here in its pure form. The experiment has shown (Fig. 2) * that the hydroxyl group spectra for both *p*-cresol and *o*-cresol are characterized by similar diffuse bands wnich are quite analogous with those of *p*-chlorophenol and explainable, in the same way as in the latter case, by strong intermolecular interaction of the hydrogen bond type. Thus, the specific effect of ortho-structure should be rejected, wherewith the assumption of intermolecular ring-closure as a cause accounting for the peculiar properties of the spectrum of *o*-chlorophenol becomes more reliable.

The further and the most demonstrative verification of our assumption was the study of the combination spectra of phenol; *p*-chlorophenol and *o*-chlorophenol solutions in various solvents. By applying neutral solvent (CCl_4) it was feasible at sufficiently low concentrations to investigate the spectra of practically isolated molecules(²). The results of these studies at volume concentrations of about 12 to 15 per cent are shown in Fig. 3 and Table 2.

Table 2

Combination Frequencies of OH Group of Phenol, *o*- and *p*-Chlorophenol Solutions in CCl_4 in cm^{-1} (12 to 15% by volume)*

Substance	Frequencies
Phenol	3603 ± 5 (line)
p-chlorophenol . .	3602 ± 5 »
o-chlorophenol . .	3540 ± 5 »

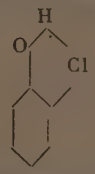
*The exciting triplet: 27388, 27353, 27293 cm^{-1}.

It follows from these data that the spectra of isolated molecules of all investigated substances are characterized by very narrow bands which even resemble lines. However; the frequency of this line in the cases of phenol and *p*-chlorophenol corresponds to ~3600 cm^{-1}, which makes a difference of about 200 cm^{-1} from the position occupied by the middle of the band in undiluted liquids (Table 1).This value is near to the frequencies of unperturbed oscillations of the hydroxyl groups of water or methyl alcohol; studied by G. S. Landsberg and collaborators in the vapour state at corresponding densities; or in solutions of low concentrations in neutral solvents (²). We have obtained a line for *o*-chlorophenol with a frequency of 3540 cm^{-1}, i. e. practically with the maximum of the narrow band which is characteristic of the hydroxyl group of liquid *o*-chlorophenol of 100 per cent purity (Table 1) and diverges by 60 cm^{-1} from the frequency of oscillation of the hydroxyl group of isolated molecules of ph nol and *o*-chlorophenol. Thus, these experiments bear witness in favour of the fact that the hydroxyl group in an isolated molecule of *o*-chlorophenol is under conditions markedly different from those that characterize the position of this group in phenol and

* The exciting triplet: 27388, 27353, 27293 cm^{-1}.

p-chlorophenol. Besides; in the case of *o*-chlorophenol the transition to isolated molecules has little effect upon the conditions of oscillation of the hydroxyl group, whereas in the cases of phenol or *p*-chlorophenol the position of the maximum of oscillations is displaced by almost 200 cm^{-1}.

These peculiarities in the behaviour of OH group in *o*-chlorophenol are fully explained by the assumption of intramolecular ring-closure in the majority of *o*-chlorophenol molecules according to the scheme:



In fact, nothing essential can happen to the structure of *o*-chlorophenol in this case of isolation of molecules in the process of dilution of *o*-chlorophenol by CCl_4 down to sufficiently low concentrations: the intramolecular ring closed

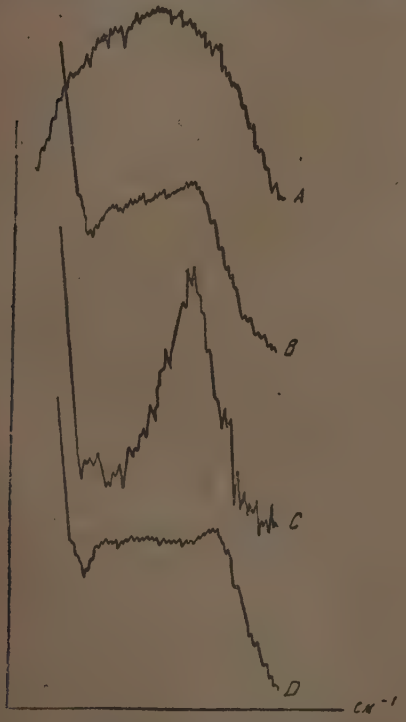


Fig. 1. *A*, water; *B*, phenol; *C*, *o*-chlorophenol; *D*, *p*-chlorophenol

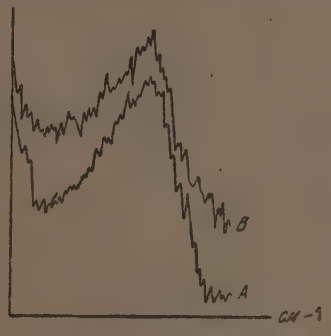


Fig. 2. *A*, *o*-cresol; *B*, *p*-cresol

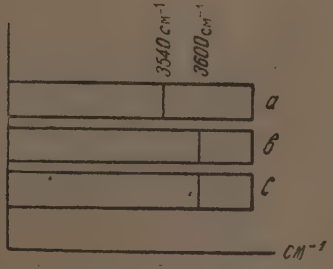


Fig. 3. *a*, *o*-chlorophenol; *b*, *p*-chlorophenol; *c*, phenol

through the hydrogen bond remains intact when the molecule has been isolated. Should the intramolecular ring exist in both liquid *o*-chlorophenol and that dissolved in CCl_4, the frequency of oscillation of the OH group may remain unaltered, which finds its expression in the coincidence of the frequencies of the sharp band maximum of the OH group in liquid *o*-chlorophenol with the frequency of the combination line of the OH group of isolated molecules of *o*-chlorophenol when diluted in CCl_4. The fact that the frequency of OH in *o*-chlorophenol is somewhat lower than that in phenol or *p*-chlorophenol, may also be accounted

for by ring-closure, since due to the latter we have to deal with O—H... Cl group finstead of OH group, the former one being practically unaltered in either the liquid phase of the pure substance or the dilute solutions. However, in the pure liquid the O—H...Cl group in a certain part of the molecules suffers some small perturbation at the expense of the surrounding molecules (apparently, from the oxygen of these molecules)(2), thus causing some expansion of the band in the liquid phase, though far less considerable than in the case of phenol or *p*-chlorophenol, since O—H...Cl in *o*-chlorophenol is an interchained group which is, on the whole, thoroughly protected from outside influence.

The intramolecular ring of *o*-chlorophenol with the weak link in the form of the hydrogen bond O—H...Cl is certainly less stable than the rings formed by valent linkages, and therefore more susceptible to external influences. On heating, for instance, ruptures of the rings are likely to occur accompanied by alteration of the spectra. Experiments of this kind are underway.

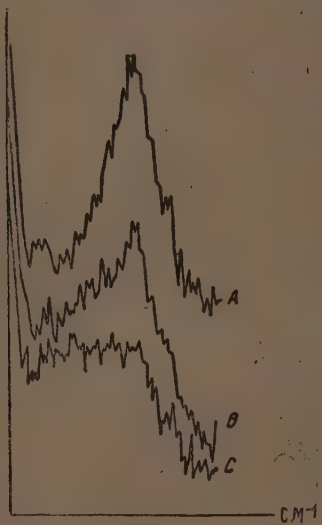
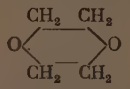


Fig. 4 *A*, *o*-chlorophlenol; *B*, *o*-chlorophenol + dioxane (12% by volume); *C*, *o*-chlorophenol + + dioxane (25% by volume)

Another possible method to influence the intramolecular ring is by the action of the surrounding molecules of the suitably selected second component. Dioxane



whose oxygen atoms have a strong disturbing effect, might be used for this purpose. The experiments we have carried out in investigating the spectra of the mixtures of *o*-chlorophenol and dioxane with 12 per cent of dioxane by volume gave the following results. When 12 per cent of dioxane are dissolved in *o*-chlorophenol, a narrow band peak with unaltered frequency of the *o*-chlorophenol band maximum (3535 cm^{-1}) is seen together with a wide band adjoining it on the side of low frequencies. With 25 per cent of dioxane in *o*-chlorophenol the peaked band with the 3535 cm^{-1} frequency disappears altogether, and there is only one wide band in the region of lower frequencies stretching from about 3280 cm^{-1} to 3575 cm^{-1} or about 300 cm^{-1} broad (Fig. 4).

The described process of alteration of the combination spectra of dioxane solutions in *o*-chlorophenol, as the concentration increases, is incontrovertible evidence that dioxane molecules have a very strong disturbing action. It is possible that we have here to deal with the process of destruction of intramolecular rings with intramolecular hydrogen bond O—H...C in *o*-chlorophenol molecules; and formation of associated complexes from heterogeneous molecules on the basis of the intramolecular hydrogen bond O—H..O. The final conclusion should be postponed till the spectra of *o*-chlorophenol and its mixtures with dioxane have been studied at various temperatures; these experiments may perhaps afford the possibility to evaluate quantitatively the respective values of the energies of the bonds.

The experimental evidence obtained in this investigation seems to confirm the assumption advanced by the author in an earlier paper, that in the main mass of *o*-chlorophenol molecules the intramolecular ring is closed by the formation of intramolecular hydrogen bond O—H...Cl*. This assumption is in complete

* As pointed out in our preceding paper, pure *o*-chlorophenol comprises 90 per cent molecules in cis-form and 10 per cent molecules in trans-form. The above considerations pertain to molecules of *o*-chlorophenol in cis-form. In the present paper we do not dwell upon the behaviour of trans-form molecules in the combination spectra.

agreement with a number of physico-chemical properties of *o*-chlorophenol, which distinguish it sharply as a typical unassociated substance due to the formation of intramolecular hydrogen bond, from the isomeric compound *p*-chlorophenol, which is an associated substance owing to the presence of monomolecular hydrogen bond([3]). At the same time the experiments have furnished support to my criticism of the theory advanced by the investigators who studied the hydrogen bond by the methods of infra-red spectroscopy (Hendrikes, Liddel, Wulff, Hilbert, Errera, Mollet, Freyman etc.): this theory leads to the incorrect conclusion that intermolecular ring-closure is absent in the case of *o*-clorophenol or similar substances([4]).

The study has been carried out on a Zeiss three-prism spectrograph with the middle camera and objective $f = 27$ cm and with relative aperture 1 : 4. The dispersion of the apparatus was 7 Å/mm for $\lambda = 4047$ Å. The spectrograms have been microphotometered with a Zeiss objective non-registering microphotometer.

The author offers his sincere gratitude to G. S. Landsberg, Corresponding Member of the Academy, for paying constant attention to this work.

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GEOCHEMISTRY

AN ATTEMPT OF HYDROCHEMICAL STRUCTURAL SURVEY AT THE AKSUBAI REGION, TARTAR ASSR

By E. A. BARS and E. S. ITKINA

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The objects of our investigations were mainly the springs of the Aksubai region, Tartar ASSR, the waters of which were subjected to chemical analysis at a field laboratory. The purpose of geochemical surveying was to establish the possible stratigraphic correlatives of the sections of rocks composing the structure, and to find out the possibility of outlining the tectonic structure on the basis of the composition of edge waters.

The surface of the area is composed by rocks not older than the Tartar stage of the Upper Permian, on the eroded surface of which lie Quaternary deposits (alluvium, deluvium, eluvium) of small thickness. On rare occasions down the slopes there occur floridine clays of Neogene (Akchagyl) age. The Tartar deposits are subdivided by the geologists who studied the region into four series in ascending order; *a*, *b*; *c* and *d*.

These series are represented by an alternation mainly of clays and sandstones. Limestones appear in the section only episodically, as it were terminating a definite cycle of sedimentation. It is along these bands that the boundary between the series is drawn. They are also the main markers of the section. The *a* series is exposed at the far periphery of the region; The apparent thickness is 9 m. The *b* and *c* series have a thickness 10 to 12 m each. The *d* series also composes a far plunge of the structure and is exposed over 40 m (according to A. P. Bludorov's data). The thicknesses of individual clay bands do not exceed 1 m; while the sandstones sometimes attain a thickness up to 10 m (in the *c* series).

The main aquifers are confined to sandstones of the *a* series; fractured limestones in the middle of the *b* series, sandstones *c* (two horizons—c_1 and c_2); sandstones of the *d* series. Aside from these; the Quaternary (mainly alluvial) deposits are also water-bearing, while the Neogene deposits are not.

There are no thick impermeable rocks in the section; on the contrary, all of the rocks are highly fractured, which fact facilitates a vertical filtration of the atmospheric waters towards the lower part of the section. The rocks of the area are poorly exposed. The country rocks are exposed in patches—in slopes of ravines and rivulets. It is to these outcrops that the discharges of springs are usually confined; these springs are utilized in a primitive way by the population. The springs of the region are associated with Quaternary alluvium and country rocks.

An examination of the table shows that the waters of the alluvium are distinguished by a high mineralization (2.4 mg equiv. to 100), contain appreciable amounts of SO''_4 (up to 0.3 mg equiv. to 100) and represent, according to their type «sulphate-sodium» waters of a formula $A_2S_2S_1$. In the formula of water after

Chemical Analysis of the Waters of Springs of the Balanda Structure, Aksubai Region

Stratigraphic horizon	Description of sample	In milligrams equivalent to 100							Fr	Palmer's characteristics					Formula of water	Type of water
		Cl	SO_4	CO_3 mg/1000	HCO_3	Ca	Mg	Na+K after difference		S_1	S_2	A_1	A_2	Ca/Mg		
Quaternary	Sample No. 103. Nagorny farm, spring at the northern end	none	0. 0	34	0.90	0.55	0.50	0.15	2.40	12.48	12,52	—	75.00	1.1	$A_2 S_2 S_1$	sulphate-sodium
$P_2^{tat}c_2$	Sample No. 4. New Balanda. Springs in the middle of the village	traces	traces	59	0.93	0.39	0.18	0.36	1.86	—	—	38.70	61.30	2.16	$A_2 A_1$	alkaline
»	Sample No. 5. New Balanda. Spring at the northern bend	»	»	28	0.66	0.42	0.21	0.03	1.32	—	—	4.54	95.46	2.00	»	»
»	Sample No. 6. Farm of the 2nd Pyatiletka Kolkhoz . .	»	»	37	0.79	0.43	0.17	0.19	1.58	—	—	24.06	75.94	2.53	»	»
$P_2^{tat}c_1$	Sample No. 126. Forestry. Spring on the stable-yard . .	none	none	33	0.92	0.37	0.33	0.22	1.84	—	—	23.90	76.10	1.12	»	»
»	Sample No. 128. New Demkino. Spring .	»	traces	31	0.65	0.24	0.18	0.23	1.30	—	—	48.76	51.24	1.33	»	»
$P_2^{tat}b_2$	Sample No. 119. Old Chelny. Spring . .	»	none	46	0.85	0.24	0.28	0.33	1.70	—	—	38.82	61.18	0.85	»	»
$P_2^{tat}b_1$	Sample No. 108. Chuv. Enoruskino. Spring	»	»	39	0.97	0.19	0.33	0.45	1.94	—	—	46.4	53.6	0.56	»	»
»	Sample No. 3. Old Mokshino. Spring at the exposure .	traces	traces	16	0.76	0.30	0.28	0.18	1.52	—	—	23.7	76.3	1.07	»	»
$P_2^{tat}a$	Sample No. 117. S. Priyutov. Spring on the right bank . .	0.03	0.38	34	0.82	0.37	0.58	0.28	2.46	22.44	10.90	—	66.66	0.64	$A_2 S_1 S_2$	sulphate-sodium
»	Sample No. 111. B. Enoruskino village. Spring downstream the village	traces	0.02	59	1.0	0.32	0.27	0.42	2.04	2.00	—	45.0	53.0	1.0	$A_2 A_1 S_1$	alkaline

V. A. Sulin; Palmer's characteristcs are arranged in the order of decreasing values.

The waters of the country rocks refer to the type of alkaline * waters of a formula A_2A_1 and $A_2A_1S_1$; are usually slightly mineralized (1.3—1.94 mg equiv. to 100) and are either deprived of sulphates, or SO_4'' is present in traces. Apart stand the waters of the oldest *a* series which contain SO_4'' in appreciable amounts; this results in a rise of the mineralization up to 2.0—2.46 mg equiv. to 100. Thus, the waters of the *a* series are distinguished stratigraphically. Among the waters of the other series, those of the c_2 series are characteristic. Correlative for these is the *r* Ca/Mg coefficient having a high value of 2—2.53, while usually it does not exceed 0.58—1.33.

The structural surveys of 1936 (by Sitnikov, geologist) and 1942 (by A. P. Bludorov, geologist) showed the existence in the region of two tectonic structures, located near the villages of Verkhnyaya (Upper) Balanda anld Chuvashskoe Enoruskino. The best studied is the Upper-Balanda structure which represents a very gently sloping anticlinal uplift with angles of dip of the order of 30°, slightly stretched in a NO direction. The eastern part of the structure is designated on maps by dotted contour lines; its structure has not been ascertained.

The relief of the country is a plane one, that is, the highest level of the marker nearly corresponds to the highest points of the relief. The catchment basins are situated within the divide elevations. Their proximity to the structure is evidenced by the well pronounced relation between the regime of the waters of the upper aquifers and the seasonal variation of the amount of precipitation.

Such a relationship of the relief, tectonics and location of the catchment basins of aquifers made us suppose that the composition of the waters tended to become higher in salts, with increasing distance from the most elevated areas of the structure towards its periphery. Such a change would be accounted for by a gradual enrichment of the infiltrating atmospheric water with mineral salts leached out from rocks, as it migrates along the bed, and in quantities depending on the length of the course of water. This working hypothesis was later on fully confirmed.

As key-horizons the c_1 aquifer was chosen for the Balanda structure and the *b* horizon for the Enoruskino structure. The choice was dictated by the number of springs confined to them and the exposure of these horizons at the surface in the arches of the structures and in their plunges. The analysis of the data obtained has shown that the waters of springs, discharging near the arch part of the structures, are distinguished by an absence of sulphates (and chlorides); while according as the structure plunges, the waters show first the traces and then appreciable quantities of sulphates.

Thus, the possibility has been confirmed of outlining the tectonic structure on the basis of data furnished by hydrochemical survey, provided definite conditions are available, and the relationships of relief, tectonics and catchment basins of aquifers are taken into consideration. It stands to reason that such a change in the composition of the waters must necessarily hold for any structure. It may be assumed in advance that in the case of a structure whose arch portion is an area of drainage rather than an infiltration zone, the springs of this arch portion will carry waters enriched with sulphates and chlorides, as compared to the waters of the peripheral parts of the structure.

A similar survey was organized by the authors in 1942 in the Bugulma region and furnished the same results.

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* Classification by V. Sulin.

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GEOCHEMISTRY

NEW TUNGSTEN DEPOSITS IN THE MIDDLE URALS

By B. KUPLETSKY

(Communicated by W. A. Obruchev, Member of the Academy, 5. I. 1943)

The Boevka wolframite deposit at the boundary of the Sverdlovsk and Cheliabinsk regions has been known since 1865; it has been repeatedly started working, and is being exploited now. When in 1930—34 special prospecting for tungsten deposits was started at the Urals along the eastern contact of the large Murzinka-Bazhenovo-Shilovo-Konev granite massif, many points were found in which wolframite and scheelite occurred, being confined to quartz veins of the granite massif. Among these points mention should be made of the deposits of the Malyshevsky and Khitny fields in the region of the Emerald mines, the Bazhenovo, Yalunin, Galochya Gora, Sosnov, Shilovo, Karassev and South-Konev deposits.

Of all the deposits listed, however, only the South-Konev proved to be of economic importance, and began to be operated since 1934 and the Karassev in 1940, while the remaining deposits were of no economic importance, presenting purely mineralogical interest.

A study of the granite intrusions of the Urals carried out by the Ural expedition of the Academy of Sciences in 1935—1940 permitted to establish the fact of the wolframite deposits of the Middle Urals being confined to the youngest phases of the granite intrusion represented by alaskite and coarse-grained pegmatite granites, developed mainly at the eastern contact of the granite intrusion.

The Karassev wolframite deposit is confined to the contact zone of white biotite medium-grained granites with hornblendic schists of the Devonian (D_2), and is located within that area of the contact where its line changes its direction from a meridional to a latitudinal one.

The dip of the contact of granites with hornblendic schists is in most cases towards the east and north-east at angles of 25 to 40°, bedded deposits and lenses of granite not infrequently occurring in the schists as a result of a lit-par-lit injection of granites into the wall rocks.

Wolframite-bearing quartz veins of the Karassev deposit fill in the granite fissures of the most varied direction and are confined both to break fractures of a latitudinal strike 290° NW and 70°NE, and to shear fractures attaining their maxima in a direction 310—325° NW and 30—55° NE.

The fact of the veins being confined to fractures of various types does not appreciably affect their composition which remains in the main unaltered. The arrangement of the veins of the Karassev ore-field shows a number of characteristic features: 1) Many fissures filled up by wolframite bearing veins lie parallel to the contacts of the granite massif, the dip of the veins incline from the contact towards the granite massif at steep angles of 75—83°. 2) The veins of

the central area form a system of arcs with their convex side turned to the north, with a dip in the northern rhumbs at an angle of 75—80°. 3) The whole of these veins outline a certain central area, as it were a funnel, towards which the tungsten-bearing veins are steeply inclined. In the central part of this annular zone there is located a stockwork zone of small gently dipping wolframite-bearing veins, with a meridional and north-eastern strike, confined to shear fractures of the granite massif. The stockwork zone stretches in a direction 285—290° NW in a comparatively narrow belt of 30—50 m; the veins having here a prevailing dip to the WNW at an angle of 20—40° and up to 65°. 4) The structure of the ore-field of the Karassev deposit is complicated by the presence of a zone of tectonic fractures of a latitudinal or NW strike; arranged in three parallel belts with which a more intense wolframite mineralization is associated: a) a northern zone with veins 49, 60—61; 72; b) a middle zone with a stockwork zone developed within it; c) a southern zone comprising veins 64, 91; 83, and outcrops of mylonitized granites along the 12th prospecting trench.

From the nature of mineralization of the quartz veins and their impregnation with muscovite, fluorite, sulphides and rarely bismuth glance and beryl, the Karassev wolframite deposit has many features in common with the Boevka and South-Konev wolframite deposits. It has; however, points of essential differences, too.

The chief of these is the lack of persistence of the wolframite-bearing veins of the Karassev deposit along the strike, and a diversity in their direction. Only a few veins are traceable to 90—100 m; while the great majority of them pinch out within 20—30 m and represent not rectilinear veins; but a system of alternating lenticular and shuttle-like swells, connected with thin stringers.

During 1942 in the region of the South-Konev Mine Administration, under the guidance of the author and M. N. Grigorev, chief geologist, large-scale prospecting and search work was organized, which by the end of the summer resulted in a discovery of two more ore-fields: the Kazakov ard the Porokhovoye.

The Kazakov wolframite-bearing area is located on the eastern contact of the Konev granite massif 1.5 km south from the Karassev deposit. At present fourteen wolframite-bearing veins have been exposed here, showing a workable wolframite content. The ore veins in this area, however; are also little persistent along the strike and have the same bead-like arrangement as the veins of the Karassev deposit; hence the wolframite reserves in the area cannot be large. A great drawback of this ore-field is its large water content and the high level of ground waters, owing to which in some veins the water appears at the depth of 0.5—1.0 m. Here it has been established that the wolframite-bearing veins have chiefly a 280—330° strike; while the veins with a NE strike abundant within the area usually carry a vitreous or smoky quartz and contain no ore.

The Porokhovoye area is located outside the granite massif, 7—8 km south of the South-Konev mine. From the traces of quartz veins on ploughing-ground here an area of about 250×150 m^2 may be outlined, in which for the first time test trenches and pipes have revealed the presence of thin quartz veins with wolframite and scheelite. The veins are located in the porphyrite-schist beds of the Upper Devonian, have a persistent 290—310° NW strike and show a good wolframite content in spite of their small thickness. From the presence of constant mica fringes in the quartz veins; and the nature of the enclosing rocks; the Porokhovoye area has many features in common with the Boevka wolframite deposit and certainly deserves attention on the part of the industry as a reserve supply of the South-Konev wolframite mine.

In conclusion it should be noted that from a personal study of the wolframite-bearing localities of the Middle Urals the following guide features for the quest for wolframite deposits in the region may be pointed out:

1) The wolframite deposits already known in the region are generally associated with the youngest phases of the granite intrusion.

2) The mightiest deposits are confined to the eastern; hanging contact of the granite intrusion; within 200—600 m from the contact.

3) The deposits located at a considerable distance from the granite intrusion and represented by quartz veins in the schist roof of the granite massif (Boevka, Zaerovo, Porokhovoye) show evidence of less high-temperature hydrothermal minerals than the high-temperature pneumato-hydrothermal deposits in granites (South-Konev, Karassev, Kazakov).

4) The quartz of the wolframite-bearing veins has a laminated platy structure; it is grey-coloured and along the lamination planes often carries manganese coats and foliae of greenish muscovite.

5) The presence of fluorite in a quartz vein is a favourable evidence for wolframite, while the presence of pyrite and limonite is unfavourable.

6) Wolframite-bearing veins often occur in the zones of greisenization of granites.

7) From the conditions of the tectonic structure of the region the most favourable for the occurrence of wolframite are quartz veins with a strike of 280—310° NW and 70—90° NE.

8) Wolframite segregations do not only occur in quartz veins, but often form independent accumulations in granite fissures.

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GEOLOGY

PROSPECTING FOR IRON-NICKEL ORES OF CAVERN TYPE IN THE MIDDLE URALS AS BASED ON GEOLOGICAL EVIDENCE

By B. P. KROTOV and A. L. YANITZKY

(Communicated by P. I. Stepanov, Member of the Academy, 3. I. 1943)

As early as the last century a number of investigators, Eremeyev (1859), Antipov the 2nd (1860), A. P. Karpinsky (1891), noted the frequent formation of deposits of brown iron ores at the contact of limestones with different magmatic rocks and crystalline schists, or among limestones not far from the rocks named, as a result of weathering process of the latter. K. I. Bogdanovich (1911) distinguished them as a type of karst deposits characteristic of the Middle Urals.

These deposits represent fillings of various-shaped and different-sized karst sinks with alluvial-deluvial deposits, in the mass of which there also occur nodules of brown iron ores and occasionally of siderite. The alluvium has been formed of an areno-argillaceous material with a greater or lesser amount of rubble of the surrounding rocks, and is stained with iron hydroxides.

The deposits of this type, occurring in limestones near or at the contact with serpentines always carry a certain amount of nickel. Such deposits containing microscopically detectable nickel hydrosilicates were named by A. P. Karpinsky the Revda type of deposits. In the past deposits containing no visible nickel hydrosilicates had been worked for their brown iron ores, but in the recent years they invited attention as nickel deposits.

The nickel-iron ore deposits of the karst type occur sporadically along the contact of serpentines and limestones within all the ridges and massifs of serpentinized ultra-basic rocks of the Middle Urals. In most places these deposits are exposed at an absolute height of 370—380 m. On the present relief of the surface the serpentines usually produce positive forms of the relief (ridges, chains) projecting above the belts of limestones and different kinds of shales, whose area of development on the relief is represented by depressions occupied by river valleys, lakes, and marshes.

Thus, the iron-nickel ore deposits are situated at those places where at a height of 370—380 m the relief begins to rise.

Geological investigations and prospecting for different minerals show concordantly that in the low portions of the present relief in river valleys, ravines and low marshy plains the surface of the Palaeozoic is covered with areno-argillaceous and rubbly alluvial-deluvial sediments whose age cannot be established with sufficient accuracy, but which are usually referred to continental Tertiary and post-Tertiary deposits. The surface of the serpentinized ultra-basic and other rocks composing the more elevated portions of the relief is covered with a weathering crust which is represented by chemical decomposition products in the lower smooth areas and by a rubble of country rocks on crests and knobs.

The surface of the Palaeozoic rocks had formerly a highly dissected relief; later on, upon a rise of the base level of erosion, it was smoothened, the lower

portions of the relief having been filled up with alluvia. At present the Urals are rising again and water courses are washing their way through the ancient sediments.

Karsts and different types of erosional depressions were formed at a considerably lower position of the base level of erosion and ground waters; upon a rise of the base level of erosion they were filled with alluvial-deluvial drift, and at the same time, the percolating solutions of iron and nickel yielded iron hydroxides, and carbonates of iron and nickel minerals were formed in them.

The conditions of karst formation and the shape of karst holes are as yet insufficiently studied. It may be presumed that they are associated with definite types of limestones, with fractured and crushed areas of limestones and serpentines, as a result of which at some places the hollows have the shape of funnels or irregular pockets; and in others, that of long slits or corridors stretching over a large distance. Karst holes are not invariably the associates of every contact of limestones with serpentines and occur only sporadically. The areno-argillaceous rocks covering the Palaeozoic in the low portions of the surface in river valleys, ravines and swampy lowlands in the area of serpentine crests, are of diverse origin. A part of them are a typical residual weathering crust on shales and limestones. Deeper down in such sediments a gradual transition in to country rocks is observed.

Another part of these rocks consist of typical deluvial and alluvial sediments, the material of which has been brought and deposited on the eroded surface of the Palaeozoic rocks and is not related to them.

The space occupied by deluvial and alluvial sediments has a depression character, with a relatively smooth relief of the surface. On the limestones and shales covered with the weathering crust but without karsts, a clear-cut negative relief is observed in the shape of a general depression of the surface. Particularly typical this negative relief is on karst limestones where there are found isolated rounded or trough-like depressions or a whole system of irregularly-shaped depressions, communicating with one another, over the generally depressed surface.

These depressions are covered by damp meadows or marshes with hillocks. As mentioned above, the brown iron ore deposits are formed in hollows in limestones within various distances from the weathering basic rocks. The iron-nickel deposits, however, which contain economic amounts of nickel, occur only in the immediate proximity of serpentine outcrops, within a distance of up to 30 m, less frequently up to 60 m.

Such deposits occur in isolated karst sunks and in a communicating system of karst depressions of various shapes in tectonically undisturbed areas, and as long slit-like holes in tectonically disturbed ones. On steep and on gradually and uniformly descending slopes the surface of the limestones is covered with alluvial-deluvial sediments of small thickness, without karst holes. At the same time, brown iron ore deposits are also lacking at such places.

Between the Nizhny Taghil and Ufaley serpentinized ultra-basic rocks (dunites and peridotites) form either detached larger intrusive bodies in the mass of a sedimentary-volcanogenous series of Silurian-Devonian age (S_2—D_1), or intrusive sill bodies stretching over a large distance. A detailed study often shows them to be a number of thin sills in this series, which on smaller-scale maps are united into continuous belts.

Upon weathering of the serpentines of this belt, nickeliferous brown iron ore deposits are formed both in the weathering crust of the serpentines themselves, and in limestones in the near-contact zone between serpentines and limestones.

When larger intrusive bodies of various shapes are present, nickel-iron ore deposits are formed under these favourable conditions in the form of a chain of detached small deposits or stretched larger deposits in the near-contact zone in limestones.

If a number of sills of ultra-basic rocks in a series of shale and limestone beds is present, nickeliferous iron ores are often formed in the karst

holes on the surface of several limestone beds between serpentine belts; or the surface of limestone patches included in a serpentine mass. Under such conditions nickeliferous brown iron ores form a whole series of closely lying deposits of the same nature. The deposits assume a still more complicated nature if on the surface of sills of ultra-basic rocks weathering crust deposits; and on the surface of the limestones, alternating with these, karst type deposits are formed. In this nickel-iron ore deposits originate, in which the mode of occurrence of the ores is different at the various parts of the deposit.

Within the area between Ufaley and Nizhny Taghil a large number of old deposits of brown iron ores are known. A part of these deposits occur in limestones near serpentinites or at the contact with them. The presence of nickel in some of these deposits has been proved. Sampling, however, was carried out without due allowance for the type of the deposits, as a result of which the data obtained can by no means be considered as characteristic of the ores from definite points.

Now it should be recognized that in all of these deposits the nickel content of ores shows a definite regularity, namely; it increases with depth and gradually diminishes with the distance from the serpentines. A chemical analysis of samples made without taking into account the above regularity can give no correct idea as to the quality of ores from different deposits. There is no doubt that the deep horizons of a part of the old brown iron ore deposits have been left non-worked because of water, and the roots of the old deposits and the spaces between them may therefore still contain considerable amouuts of iron-nickel ore.

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PLANT PHYSIOLOGY

ON THE VEGETATIVE PROPAGATION OF THE RUBBER PLANTS KOK-SAGHYZ, TAU-SAGHYZ AND KRYM-SAGHYZ*

By G. KH. MOLOTKOVSKY

(Communicated by A. A. Richter, Member of the Academy, 9. IV. 1943)

It is only a very short time ago that kok-saghyz, krym-saghyz and tau-saghyz plants bearing rubber in their root, were introduced into cultivation, and, therefore, many of their biological peculiarities have been very scantily investigated.

Their vegetative propagation belongs to the problems whose development has but lately been started. By using cuttings as a method of planting it is possible, especially in the case of kok-saghyz, to obtain rapid and simultaneous growth, which is not always the case when seeds are used for planting. T. D. Lyssenko has suggested the propagation of kok-saghyz by root fragments (1). Among literary information on the subject one finds a preliminary experiment on the vegetative propagation of kok-saghyz attempted by Minbaev (2).

The importance of this problem and the fact that it has been but poorly investigated have prompted the present author to explore it first of all at Alma-Ata; and afterwards in the other regions of Kazakhstan. The experiments were made in 1942 in the months of April, May and September, according to the following method.

The roots of kok-saghyz, 2, 3 and in some cases 12 hours after they had been dug up from the soil, were cut up across into fragments 1.5 to 2 cm in length. These fragments were then planted into the following substrata: sand, peat, humus, and humus with sand. They were made to germinate in boxes at 14—18°C. Cool hot-beds were also tried for this purpose in parallel tests with the same substrata.

After a period of 4—12 days, according to the substratum, the formation of callus was observed on the cuts of the fragments. From 2 to 10 days later, green sprouts made their appearance in the apical part of the root fragments. As soon as they attained a length of 1—1.5 mm in 20—25 per cent of the cuttings they were planted by hand in the vertical position, and the soil was made compact around each of them. Grey soil or light chestnut soil, fall-ploughn, was used. Harrowing preceded planting. The fragments were planted in rows at a distance of 10 cm from one another, to a depth of 2—3 cm. The area of one experimental plot was 20 m^2. There were three replicates in every test. In one of the sets the watering was made in furrows, in the other with a pot provided with a net. The water was supplied at the approach of the evening, and the next day the soil was loosened according to the extent of the moisture.

In the main, negative results were obtained in all sets, except that there were cases when the upper part of the root, the so-called head consisting of the root-

* Report delivered in a plenary session of the Scientific Board of the W. R. Williams Institute for Agricultural Research, Kazakhstan, on January 20, 1943.

crown and the adjoining small portion of the root; showed a good rooting response.

The rest of the root continued to lie in the soil, and nothing but coagulations, or small green sprouts 2—4 mm long, at the best, had formed on the cuts. Only in isolated instances did these green sprouts appear above ground. After 1.5—4 weeks the cuttings began to wither, and gradually died away, because no root formation had taken place in spite of the great care exercised in keeping up optimal conditions of humidity, aeration, etc. In some cases the root fragments showed signs of rotting 5—10 days after they had been introduced into the soil, and soon they died off.

Similar results were obtained in the tests of 1941, carried out in the 16th Party Congress Collective Farm of the Sarkand district; Alma-Ata region, and in the experimental field of Bostandyk; South Kazakhstan. In all tests one and two year old plants of kok-saghyz were experimented upon. It is worthy of note that the first showed, none-the-less, a high viability.

As pointed out earlier, the root crown with the adjoining portion of the root (the root head) showed better rooting compared to the lower portions of the root. Those from two year old specimens even formed fruit in the majority of cases.

In this connexion it was necessary to trace in more detail the rooting of such heads; in view of it being possible to use them as planting material under industrial conditions. In the case of decapitation of kok-saghyz, krym-saghyz and tau-saghyz roots the remaining part is not lost in the soil, but rather regenerates a new leaf apparatus; if the conditions are favourable, and even bears flowers in the same year if the age of the plant permits this. The fact that the decapitated plants make further growth is of special interest, because it is encountered rarely in plants grown for their root, in which class our rubber plants belong.

To complete the picture, other plants with rubber-bearing roots were tested, viz. tau-saghyz and krym-saghyz. The experiments with these plants were made in June under field conditions with artificial water supply. Grey soil. Kok-saghyz was tested in August. Decapitation was done with a garden-knife. The cuttings (heads) were of different size, from 0.5 to 2.5 cm. Only in the case of kok-saghyz was it possible in most cases to obtain a material of uniform length, ranging from 1 to 2 cm. The root fragments were planted with 2/3 of the leaves cut-off. They were planted in the soil vertically, with the aid of a Kolesov's sword, and the soil was pressed to the cuttings. The plants were cared for in the usual way.

The data characterizing the rooting response of the rubber plants tested are given in Table 1.

It may be seen from the figures of Table 1 that the best results with regard to rooting were obtained with krym-saghyz, 88 per cent. Then follows kok-saghyz with 65 per cent, and finally tau-saghyz, which almost utterly failed to form roots under the given conditions. Some cuttings of the latter formed a good callus and occasionally sent forth even green sprouts, 1—2 mm long, which perished within an interval of 7—20 days.

Table 1

Rooting of Kok-saghyz, Tau-saghyz and Krym-saghyz Root Heads under Field Conditions

Name of plant	Age	Time of taking and planting the specimens	Number of root heads			Appearance of regenerates		Number of fruiting plants		Plants that passed into winter season	
			Planted	Rooted							
				Abs.	%	Isol.	Mass	Abs.	%	Abs.	%
Tau-saghyz	Two years	22.VI	800	—	—	—	—	—	—	—	—
Kok-saghyz	One year	18.VIII	4167	2709	65	24.VIII	31.VIII	124	2.9	2560	67
Krym-saghyz	»	22.VI	3600	3168	88	30.VI	6—10.VII	2560	71	2996	83

As regards regeneration of the decapitated roots left in the soil, nearly the same picture is observed. First place is held by krym-saghyz, second by kok-saghyz, and the third by tau-saghyz. The only difference is that in this test the decapitated roots of tau-saghyz did not perish; but continued to restore the leaf rosette lost. The results obtained are summarized in Table 2.

Table 2

Influence of Decapitation of Kok-saghyz, Tau-saghyz and Krym-saghyz under Field Conditions on the Ability of Regenerating Roots Left in the Soil

Name of plant	Age	Time of decapitation	Appearance of regenerates		Number of plants			Plants that passed into winter season	
			With soil cover	Without soil cover	Decapitated	Regenerated	%	Abs.	%
Tau-saghyz	Two years	22.VI	12.VII	16.VII	850	493	58	325	38
Kok-saghyz	One year	18.VIII	24.VIII	28.VIII	4500	3150	70	2900	64
Krym-sagyz	»	22.VI	5.VII	2.VII	3800	3572	94	3354	88

On decapitation the exudation of latex was especially abundant in the case of tau-saghyz. The film formed covered the surface of the cut rather tightly; which did not, however, prevent the sprouts from making their way through it.

From the cuts uncovered with soil the sprouts appeared in a better condition and in shorter time, than from covered cuts; although the soil cover was not above 1 cm thick. Covering with soil, which had been aimed to shade the cuts, resulted in a similar behaviour of kok-saghyz and krym-saghyz plants as regards the regeneration of their leaf rosettes.

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EVOLUTIONARY MORPHOLOGY

ON THE TRANSFORMATION OF THE VALVES OF *SINUS VENOSUS* OF THE HEART IN THE PROCESS OF ITS DEVELOPMENT IN HIGHER MAMMALS AND IN MAN

By W. N. SHEDENOW

(Communicated by L. A. Orbeli, Member of the Academy, 12. IV. 1943)

When studying the onto- and phylogenesis of the heart in higher mammals and in man, more strictly, of its *sinus venosus*, one of the most interesting and important questions we are confronted with is that of the transformation of the sinus valves (*valvula venosa dextra et sinistra*). Unlike in man whose right valve assumes during the embryonic period a particular significance, transforming into the Eustachian and the Thebesian valve; in most of the higher mammals it is reduced like the left one, without undergoing any special transformation ([1], [2]). We have also shown ([3],[4]) that in man the transformation of the right *valvula venosa* into the Eustachian and the Thebesian valve is no natural course of the reduction process and no simple cleavage of the valve, but a secondary specific and active process, determined in the course of its history and proceeding at a higher level of the evolutionary development of the heart than in animals.

The above-said is essential, for up to the present time the difference in the processes of transformation of *valvulae venosae* in man and animals has never been stressed. As a result, the existence in animals of an Eustachian and a Thebesian valve received an arbitrary and mostly incorrect interpretation.

Morrill ([5]); Zietzschmann ([6]) and Gätzi([7]) were the first to pay attention to some differencies in this respect between animals and man, but they draw no a definite and correct conclusion.

As material for our investigation we made use of a large number of hearts of various animals: *Ungulata*, *Ruminantia*, *Omnivora*, *Carnivora*, *Rodentia*, as well as of human hearts, all at various embryonic and post-embryonic stages of development; examined with the help of a Zeiss magnifying glass.

Our investigations have shown that the transformation of *valvulae venosae* and their ultimate formation proceeds in the following way. The transformation of the left sinus valve consists both in man and animals in its gradual reduction. As a rule, the reduction proceeds here at a higher rate than in the right valve (in those cases when the latter undergoes reduction like the left one). The reduction of the left valve goes on more quickly and is sooner achieved in its superior-anterior section, encircling the mouth of the Lower-sack from the left and passing back through the upper sinus wall (place of the future formation of *tuberculum intervenosum*; s. Loweri). Unlike this, its posterior-inferior section is the last to be eliminated, taking part, upon the disappearance of *spatium interseptovalvulare*; in the formation of the inferior edge of *foramen ovale*. After the mouths of the two *v. cavae* have been formed and divided, the atrophying left valve takes

on an elongated sigmoid shape. The rôle of the left sinus valve in the process of its transformation is no important one.

Much more important and interesting are the transformations of the right sinus valve. As we have already said, they are not like in man and the animals. In man the right sinus valve in its upper third undergoes total reduction; similar to the left one. In the other two thirds it is subject to no reduction; but on the contrary, to secondary and specific development of its sections. In its middle part the sinus valve undergoes particular changes, and assumes a specific importance for the regulation of the blood flow from *v. cava inf.* into *for. ovale*, being transformed into the Eustachian valve. In its inferior third, the valve transforms into the Thebesian valve, preventing the regurgitation of the blood into the mouth of *sinus coronarius*. The specific features of the transformation of the right *valvula venosa* into these valves consist in its altered shape and in the development of the corresponding sections. It proceeds in the following way. In the region of *sinus septum inf.* (partition between *v. cava inf.* and *sinus coronarius*), near its external end adjoining the valve on the latter appears a kind of constriction subdividing it into the two sections mentioned. These sections undergo secondary development, while their contiguous ends adjacent to *sinus septum* seem to fuse with the latter, bending inwards and entirely separating from each other. The upper, larger part of the valve causes by its lower end the formation of the endocardial fold along the upper wall of *sinus septum*; this constitutes a prolongation of the valve proper and is directed towards the inferior-anterior section of *for. ovale*. The Eustachian valve formed in this way is, in accordance with the circumference of *v. cava inf.* it encircles, large, well developed in height, especially in its middle part, and crescent-shaped. The lower section of the right valve is correspondingly prolonged inwards, along the lower wall of *sinus septum*, entirely separating from its upper section, and transforming into a crescent-shaped valve situated in the external angle of *sinus coronarius* (Thebesian valve). It is much smaller and more delicate than the Eustachian valve, its character approaching that of the common veinous valves. It is preserved throughout the life, without being deformed, while the Eustachian valve is subject to gradual involution.

As pointed out above, in animals the transformation of the right *valvula venosa* does not lead to the formation of an Eustachian and a Thebesian valve. In most of the animals this is accounted for by a compensatory substitution of the functions: of those of the Eustachian valve, by *limbus for. ovale* (in some animals together with *tub. intervenosum*), and of those of the Thebesian valve, by the lower *sinus septum*.

Two types of transformation should by distinguished in the right *valvula venosa*. In most animals the right valve undergoes gradual reduction upon the fusion of *sinus venosus* with the auricle proper, without suffering any secondary alteration. In the auricle already formed the valve has the shape of a moderately high endocardial fold (sometimes undulatory), encircling from the right the mouth of the anterior and posterior *v. cavae* and *sinus coronarius*. It originates from the anterior section of the mouth of *v. cava cran.*, ending downwards from the mouth of *sinus coronarius*, near its internal angle (below the anterior-inferior angle of *for. ovale*). Like the left valve, it assumes the shape of an irregularly elongated *S*. It does not separate into isolated sections according to the mouths of veins encircled by it, and forms therefore no valves. The process of the atrophy is more clearly expressed in the upper third (near the mouth of *v. cava cran.*), where it is achieved sooner than in the other parts. In the remaining two thirds the valve is homologous as to its origin to the human Eustachian and Thebesian valves taken jointly, without being their functional analogue. The valve becomes sooner atrophied near the mouth of *v. cava caud.*; the last to undergo atrophy is its part near the mouth of *sinus coronarius*, where its noticeable vestiges may often be detected. This type of transformation of *valvulae venosae* consisting in their reduction without any secondary alteration, is peculiar of most animals. The reduction of the valves may be achieved at a rather early stage of their

embryonic development, which takes place in animals with a long period of pregnancy, or at later stages, even during the post-embryonic period in animals with a short period of pregnancy. In these it may remain unachieved, leaving traces of the right valve in the shape of a low crest.

In some animals the right *valvula venosa* like the left one partly undergoes some secondary alterations, without suffering reduction during the embryonic period. The right valve which is usually situated in the region of the inferior *sinus septum*, splits off a fold along its upper wall, towards the anterior-inferior angle of *for. ovale*. It looks as if the valve in its lower third woud cleave at an angle into two folds, the one being its direct prolongation (below the mouth of *sinus coronarius*), and another towards *for. ovale* along the usual path of the Eustachian valve in man (above the mouth of *sinus coronarius*). The latter is usually better developed than the lower one which is rather delicate. At the first glance a deceitful impression is created of these valves being identical to the Eustachian and Thebesian valves in man. As a matter of fact, these valves are only their homologues by origin, without being analogous by shape, and, consequently, are not identical with them. This is evidenced by the following: 1) the upper end of the right valve is not bounded by the mouth of *v. cava caud.* (as the Eustachian valve is), but proceeds, like the left one, to the mouth of *v. cava cran.*; 2) the lower end of the valve is not subdivided into two plates (which takes place in the Thebesian valve), but encircles the whole of its lower end in a way analogous to the primitive *valvula venosa dextra*; besides, it becomes gradually reduced during the post-embryonic period.

The transformation of *valvulae venosae* of the heart in higher mammals thus proceeds in three principal ways: 1) by way of a total reduction of the two valves without any secondary changes and functional significance (*Ungulata, Ruminantia, Omnivora, Carnivora*); 2) by way of partial secondary alterations of the right valve, leading to a cleavage of its inferior end and to a formation of a kind of prototype of the Eustachian and Thebesian valve (*Rodentia*); 3) and, finally, by way of specific secondary alterations of the right valve, leading to a formation of special heart lids, the Eustachian and the Thebesian valve in man.

The Eustachian and Thebesian valves in man, according to BNA (1895) and INA (1935), are named *valvula venae cavae inferioris* (Eustachii) and *valvula sinus coronarii cordis* (Thebesii). As regards the animals, it should be pointed out that in those of them whose *valvulae venosae* undergo reduction (type I) their deformed remains are to be confounded neither with *valvula venae cavae inf.* nor with *valvula sinus coronarii* (in particular, in *Carnivora*) which do not arise at all. In the animals, however, whose *valvulae venosae* undergo partial secondary alterations (type II), the terms: *valvula venae cavae caudalis* and *valvula sinus coronarii cordis*, according to our opinion, can be conventionally admitted in so far as they exist (the latter, as well as the former undergoes reduction in the post-embryonic life); however, they are not to be identified with the Eustachian and Thebesian valves in man.

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